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## Canadian Journal of Chemistry

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## SYNTHESIS, REACTIONS, AND PROPERTIES OF SOME HIGHLY HINDERED DIPHENYL ETHERS<sup>1, 2</sup>

MARJORIE ALLEN<sup>3</sup> AND R. Y. MOIR

### ABSTRACT

In the Hems synthesis of diphenyl ethers, an ortho-carbonyl offered less obstruction when held in a lactone ring than when present as an ester. Side reactions interfered with the Hems synthesis of highly hindered diphenyl ethers, and the highly hindered, highly activated ethers produced in the synthesis were easily cleaved by nucleophilic reagents, often in a few minutes at room temperature. The latter fact added a lively interest to the transformation of the ethers into other derivatives. Three of these were of special interest: (a) methyl 2-(6'-amino-4'-carbomethoxy-2'-nitrophenoxy)benzoate (V1c) which existed in remarkably stable dimorphic forms, (b) the dibenzoxazepine VIII, and (c) the quadruply orthosubstituted, unsymmetrical 7-(4'-carbomethoxy-6'-laevo-menthoxycetamino-2'-nitrophenoxy)metameconine (IX). Attempts to isolate diastereoisomeric substances having the diphenyl ether link as an element of asymmetry failed, the classical explanation of the low configurational stability (due to bending and twisting of bonds) being superior to the quantum mechanical explanation of a tunnelling oscillation of oxygen.

This paper describes the synthesis of diphenyl ethers bearing three or four groups ortho to the ethereal linkage, their conversion into unsymmetrical derivatives, and our tentative conclusion that the unsymmetrical derivatives cannot be resolved into optical isomers at room temperature. The most interesting part of the paper describes the synthetic methods that must be used in the face of the very great ease of disruption of the ethereal linkage.

### Synthesis of Hindered Diphenyl Ethers

Ullmann's reaction (1, 2) is not very useful for the synthesis of hindered diphenyl ethers<sup>4</sup> (3, 4, 5, 6, 7, 8, 9). A more powerful method is the well-known reaction of a phenol, a base, and an activated aryl halide (10, 11, 12). Considerable activation is required in the aryl halide: with low activation, as with *p*-fluoronitrobenzene, the reaction occasionally fails with as few as two ortho substituents (13), but with greater activation successes with three ortho groups are common, and using the great activation of picryl chloride, Dahlgard and Brewster (14) recently succeeded in making two quadruply orthosubstituted diphenyl ethers. In this method, the large number, position, and similarity of the activating groups required are an embarrassment in further synthetic steps. A more promising synthesis discovered by Borrows, Clayton, Hems, and Long (15) has as its essential step the reaction of a phenol with an activated N-phenylpyridinium salt.

One main advantage of the new method is its lower requirements for activation (9, 15). The discoverers of the reaction felt that at least two nitro groups were required, but

<sup>1</sup>Manuscript received July 6, 1959.

Contribution from the Department of Chemistry, Queen's University, Kingston, Ontario.

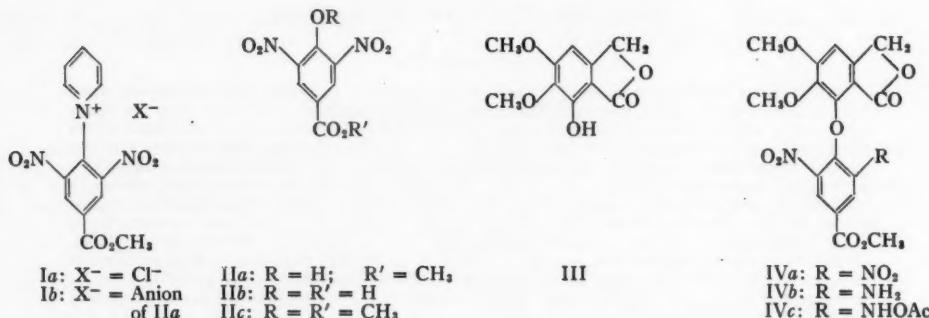
<sup>2</sup>Most of the material is taken from a thesis written by Mrs. Marjorie Allen at Queen's University in April, 1959, in partial fulfillment of the requirements of the degree of Master of Arts. Some (referred to this footnote) is taken from a paper given by R. Y. Moir at the Symposium in Organic Chemistry of the Chemical Institute of Canada at Montreal, March 9, 1954.

<sup>3</sup>Canadian Industries, Limited, Fellow, 1958-59.

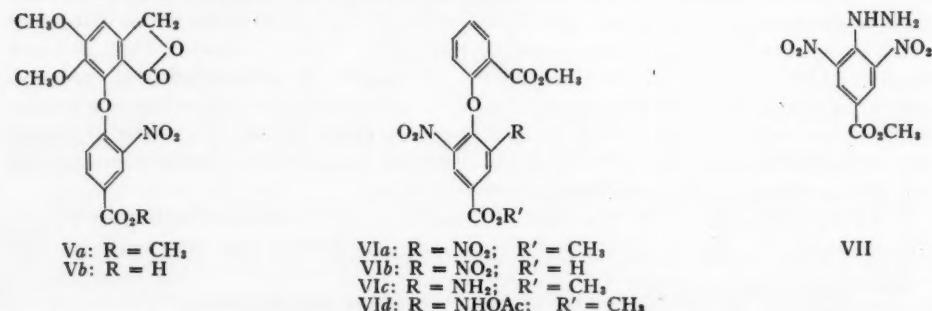
<sup>4</sup>See footnote 2.

McRae, Moir, Ursprung, and Gibbs (9) and at almost the same time Grundon and Perry (16) showed that activation by one nitro and one carbomethoxy group sometimes sufficed. Constantin and L'Écuyer (17) later showed that one nitro and one formyl group were sufficient in several instances. This theoretically small extension of the limits of activation has already been of considerable service to those interested in the synthesis of cularine and the bis-benzylisoquinoline alkaloids (9, 16, 17, 18).

The new synthesis may produce highly hindered diphenyl ethers with fantastic ease from moderately activated reactants. Thus N-(4-carbomethoxy-2,6-dinitrophenyl)-pyridinium chloride (Ia) with 7-hydroxymetameconine<sup>5</sup> (III) gave the maximally orthosubstituted ether IVa, while the slightly activated N-(4-carbomethoxy-2-



nitrophenyl)pyridinium tosylate reacted easily with III to give the triply orthosubstituted ether Va (9). In this paper it is shown that Ia reacts with methyl salicylate to give the triply orthosubstituted ether VIa with ease. Nevertheless, since 1952 we have accumulated many more failures than successes with the method. For example, methyl salicylate, which smoothly reacts with Ia, has repeatedly failed to react with the less activated N-(4-carbomethoxy-2-nitrophenyl)pyridinium tosylate, which in turn reacts smoothly with III. These examples must closely illustrate the lower limit of activation for ortho-carbomethoxydiphenyl ethers (compare reference 17).



One new side reaction is conveniently described here. In the new preparation of VIa, as well as in the repetition of the synthesis of IVa, the same quaternary salt, N-(4-carbomethoxy-2,6-dinitrophenyl)pyridinium 4'-carbomethoxy-2',6'-dinitrophenoxide (Ib) was

<sup>5</sup>The numbering scheme for the metameconines is that of Chemical Abstracts. A different scheme was used in our previous papers in this journal.

isolated in considerable yield. Its proof of structure by synthesis and degradation is described in the experimental part. Quaternary salts have previously been isolated from two sources in the synthesis: (a) from a simple double decomposition of the ionic reactants, or (b) from a nucleophilic attack of pyridine upon an activated diphenyl ether (the reverse of the synthetic reaction) (19). The salt *Ib* must have arisen in still a third way, the simplest explanation being that it arose from the hydrolysis of the very unstable reactant *Ia*, probably during the isolation of the products. If this explanation is correct, then water attacks *Ia* at the 1-position of the benzene ring, while hydroxide ion attacks it at the 2-position of the pyridine ring (see Experimental section) (20), a conclusion that raises the most interesting questions about the mechanism of the synthesis.

Other side reactions will be reported in a later paper, together with the limitations they set upon the scope of the synthesis.

#### *Reactions of Highly Hindered, Highly Activated Diphenyl Ethers*

Nucleophilic scissions of the ethers described in this paper occur with remarkable rapidity; apparently a considerable energy of steric compression aids the well-known effects of activation (11). The experimental methods described below were designed to avoid disruption of the sensitive ethereal linkages while (a) introducing asymmetry into the molecules or (b) hydrolyzing ester groups to free carboxyl groups with a view to possible resolutions.

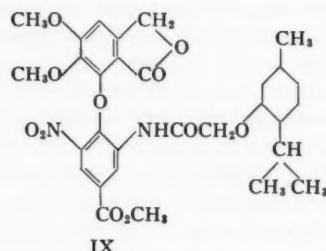
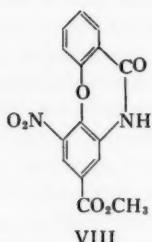
The ether *Va* is readily cleaved by alkali (9) but careful control of the conditions of saponification has now been found to give the free acid *Vb* in very high yield and purity. With the more highly activated ether *VIa*, good yields on saponification were no longer possible. The best yields of the free acid *VIb* were given by 5 minutes' contact of *VIa* with aqueous potassium hydroxide at room temperature; scission of *VIa* was easily detectable after only 1 minute's contact! The conditions which served to give excellent yields in the saponification of *Va* completely degraded *VIa* to the phenolic acid *IIb*.

With more nucleophilic reagents it was not possible to prevent nucleophilic attack upon the ether. Methoxide ion (provided by barium hydroxide in methanol) degraded *VIa* without saponification to the ester *IIc* in 3 minutes at room temperature. (The reagent was shown to be capable of saponifying *IIa* to the barium salt of *IIb*.) Hydrazine and Raney nickel gave the phenylhydrazine *VII* without concurrent reduction of the nitro groups.

Selective reduction of one nitro group was achieved with iron and acetic acid. The ether *IVa* was reduced to *IVb*, and the ether *VIa* to *VIc*. These very fortunate reductions provided the asymmetry needed for possible resolvability. Each of the amino esters was characterized through its acetyl derivative (*IVc* and *VID*, respectively). The amino ester *VIc* exhibits a dimorphism remarkable in that both forms sometimes crystallize together spontaneously from the same mother liquor. The very reproducible double melting point is shown in Plate I.

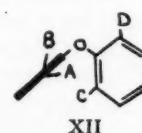
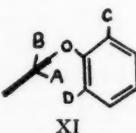
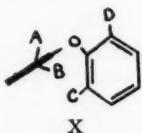
When the amino ester *VIc* was heated to 210°, it was converted into its lactam (VIII), which was also produced more directly by the reduction of the dinitro ester *VIa* with stannous chloride in the presence of hydrochloric acid. The interesting ring system of VIII (21) is accompanied by substituents well placed for further synthesis. It might be added that the formation of VIII and of the monoacetyl derivatives *IVc* and *VID*, the scissions of the ethers, and the methods of synthesis provide unequivocal proofs of the structures suggested in this paper and the previous one (9).

The amino ester *IVb* was converted into its N-laevomethoxyacetyl derivative *IX*, the farthest step in our development of the chemistry of metameconine (8, 9, 22), and the most highly hindered asymmetrical diphenyl ether we have yet been able to produce.



#### Resolvability of Highly Hindered Diphenyl Ethers

Many years ago it was suggested<sup>6</sup> on the basis of a study of models (9) that suitably hindered diphenyl ethers might be resolvable into optical isomers. During the course of our work, Dahlgard and Brewster (14) reported their failure to resolve an unspecified highly substituted diphenyl ether. They further suggested that such a resolution might be theoretically impossible if there exists a "tunnelling" oscillation of the ethereal oxygen analogous to the oscillation that destroys asymmetry in substituted ammonias. That was not our independent appraisal of the problem, and a study of the models shows that inversion with the allowed rotations converts a diphenyl ether into itself.



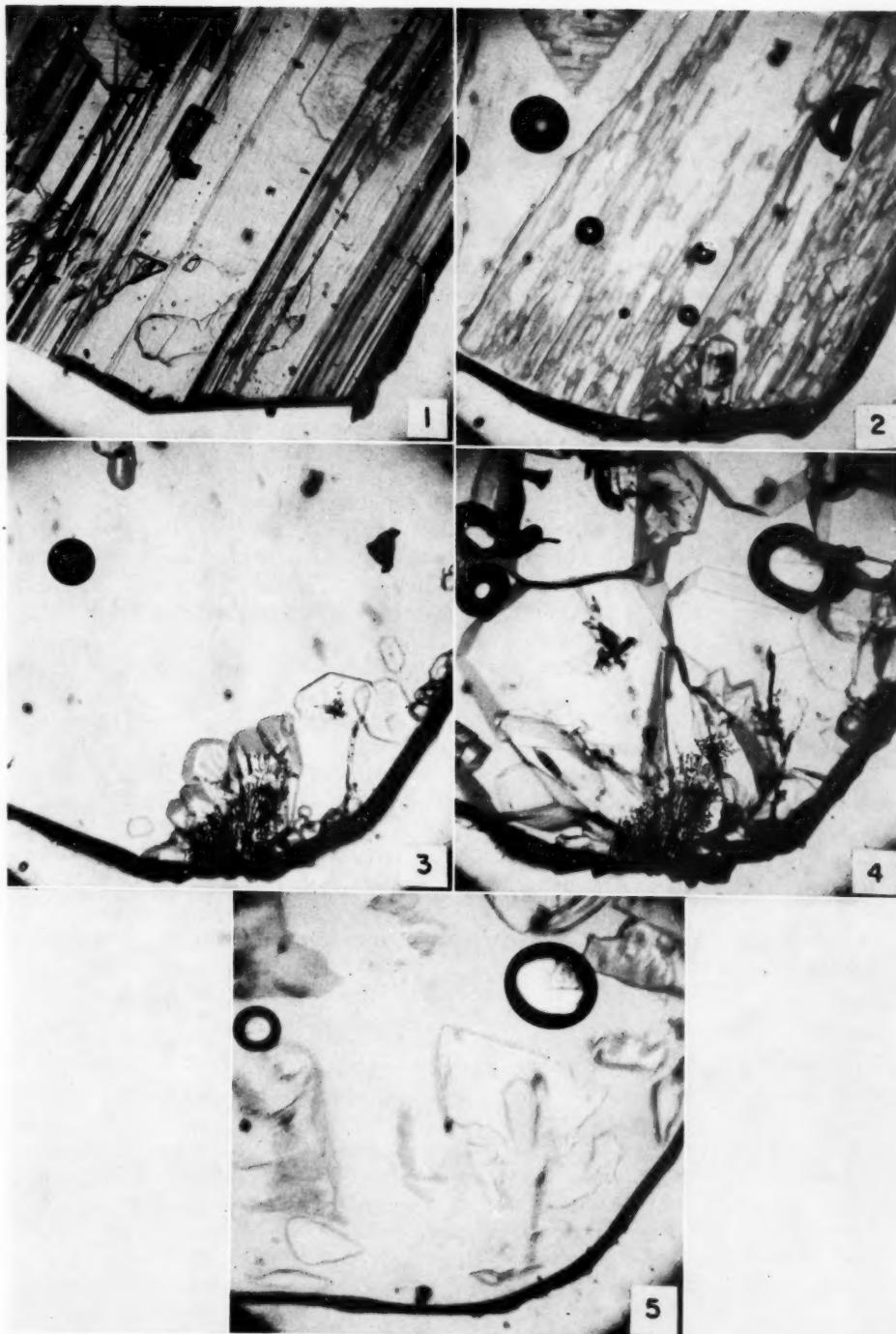
In compound X, A is behind the plane of the paper, and B is in front. Inversion through oxygen converts X into XI, while concerted rotation of the two benzene rings about the oxygen bonds converts XI into X. Neither X nor XI can be made to coincide with XII, the mirror image of X, unless interfering groups are forced past each other.

However, we have failed to separate into diastereoisomers either the brucine salt of Vb, or the much more highly hindered amide IX. Moreover, neither of these compounds exhibited any mutarotation in solution, so that apparently even the lower order of configurational stability, observed by Adams and his co-workers (23) for slightly hindered diphenyls, is absent. Dahlgard and Brewster (14) showed that increasing orthosubstitution of diphenyl ethers is accompanied by the gradual disappearance of absorption bands near 3000 Å in the ultraviolet spectra. They felt that this was due to the growing lack of coplanarity between the benzene rings with the consequent loss of quinonoid resonance, and they concluded that rotational isomers of diphenyl ethers do exist, though they may not be sufficiently stable to be isolated as such. The triply orthosubstituted ether Va showed marked absorption near 2900 Å, while the maximally orthosubstituted ethers VIc and IX showed only very weak bands near 3550 Å and 3250 Å, respectively. Accepting the interpretation of Dahlgard and Brewster does lead to the reasonable conclusion that

<sup>6</sup>See footnote 2.

FIGS. 1-5. Dimorphism of methyl 2-(6'-amino-4'-carbomethoxy-2'-nitrophenoxy)benzoate (VIc).  
 FIG. 1. "Plate" form at room temperature. FIG. 2. "Plate" form melting at 135°, with the "prism" form already beginning to grow in the melt. FIG. 3. Growth of "prism" form, 136-141°. FIG. 4. Complete solidification at 141°. FIG. 5. Melting of "prism" phase at 144-145°. (Photomicrographs by Professor J. R. Allen.)

PLATE I





there is little steric interference with coplanarity in *Va*, but that there is marked interference in *VIc* and *IX*.

#### EXPERIMENTAL

Melting points, unless otherwise stated, were determined in an instrument of high precision (24). Melting points followed by (k) were performed on a Kofler Micro Hot Stage and lowered 3–5° to agree with precision capillary melting points within less than 1° up to 250°. Uncorrected melting points were determined in the Fisher–Johns apparatus; comparison with the precision apparatus at one point near the center of the range used here showed the instrument to read about 3° high. Infrared spectra with one exception were done with potassium bromide disks containing 0.8% to 2% by weight of the sample. Ultraviolet spectra were determined with the Beckman recording spectrophotometer. Pyridine was heated under reflux with barium oxide, distilled from the barium oxide, and stored over fresh barium oxide.

#### 7-(4'-Carbomethoxy-2'-nitrophenoxy)metameconine (Va)

A repetition of the previous procedure (9) showed that no by-product of the type described below (see under *IVa*) could be isolated.

#### 7-(4'-Carboxy-2'-nitrophenoxy)metameconine (Vb)

The methyl ester (*Va*) (5.52 g) was mechanically stirred at 76–81° for 30 minutes with a solution of potassium hydroxide (2.9 g) in water (30 ml) and 95% ethanol (30 ml). The solution was immediately cooled and acidified; the fine needles which slowly deposited were recovered, washed, and dried; yield 88%, m.p. 236.0–237.8°. Two recrystallizations from dilute acetic acid gave the analytical sample of *Vb*, m.p. 237.4–238.4°, in agreement with the indirectly characterized material previously obtained (9). Found: C, 54.28; H, 3.52%. Calc. for  $C_{17}H_{18}O_9N$ : C, 54.40; H, 3.49%.

The *brucine salt* of this acid was subjected to three lengthy fractional crystallizations from acetone and from methanol; the salt fractions all showed similar, wide, melting ranges with unsatisfactory upper limits, and their habits varied. A typical fraction of the salt (3.03 g) had m.p. 174.5–177.5° (uncorr.), and  $[\alpha]_D^{21} = -7^\circ$  (in chloroform), with no mutarotation at all in the period of 4 to 71 minutes after formation of the solution. Free acid was liberated from the salt by very cautious acidification in the cold of initial, central, and final fractions, but all the acid fractions had zero rotation. Attempts were also made to induce spontaneous crystallization of one enantiomorph of the free acid, using new apparatus free from scratches, great precautions to destroy random seeds, and seeding from single, well-formed crystals with early interruption of the recrystallization process, but all the attempts gave acids of zero rotation.

#### 7-(4'-Carbomethoxy-2',6'-dinitrophenoxy)metameconine (IVa)

A repetition of the previous experiments (9) showed the presence of a by-product. Methyl 4-chloro-3,5-dinitrobenzoate (*Ia*) (1.65 g) (15) and dry pyridine (10 ml) were warmed on the steam bath for 5 minutes, the pyridinium salt separating as crystals. 7-Hydroxymetameconine (*III*) (1.35 g, m.p. 158–159°) (9) was added and the heating continued for 90 minutes. The deep red solution was poured onto ice and the product, which soon solidified, was recovered, dried, and recrystallized from acetone to give a mixture of (a) pale yellow prisms, and (b) long, deep yellow needles. The products were separated mechanically by swirling away the lighter needles in the acetone mother liquor, a process which greatly simplified the subsequent purifications. After a second recrys-

tallization from acetone the prisms gave 1.4 g of pure 7-(4'-carbomethoxy-2',6'-dinitrophenoxy)metameconine (IVa), m.p. 210-211° (k). Found: N, 6.55%. Calc. for  $C_{18}H_{14}N_2O_{11}$ : N, 6.45%. The crystals were stable in air (cf. ref. 9), but they were decomposed by light.

The yellow needles, after another recrystallization from acetone, melted at 240-242° (uncorr.). They are shown below to be N-(4-carbomethoxy-2,6-dinitrophenyl)pyridinium 4'-carbomethoxy-2',6'-dinitrophenoxyde (Ib).

*7-(6'-Amino-4'-carbomethoxy-2'-nitrophenoxy)metameconine (IVb)*

Iron powder (0.27 g) was heated on the steam bath for 1 hour with a solution of 7-(4'-carbomethoxy-2',6'-dinitrophenoxy)metameconine (IVa) (1.0 g) in glacial acetic acid (60 ml). The mixture was evaporated to dryness and the residue thoroughly extracted with water and then with boiling methanol (100 ml). A yellow powder (0.4 g), m.p. 230-233° (k) was thus obtained; two recrystallizations from acetone gave the analytical sample, m.p. 234-235° (k). Found: C, 53.63; H, 3.99; N, 7.18%. Calc. for  $C_{18}H_{16}O_9N_2$ : C, 53.47; H, 3.96; N, 6.93%.

*7-(6'-Acetamino-4'-carbomethoxy-2'-nitrophenoxy)metameconine (IVc)*

The above amino compound (IVb) (0.1 g) was heated 5 minutes with acetic anhydride (2 ml) and concentrated sulphuric acid (1 drop). The solution was poured into water and boiled to decompose the acetic anhydride. White needles, m.p. 197-199° (k) were deposited from the cooled solution. Two crystallizations from 50% aqueous methanol raised their m.p. to 206-207° (k). Found: C, 54.16, 54.14; H, 4.14, 4.02; N, 6.08, 6.50%. Calc. for  $C_{20}H_{18}O_1N_2$ : C, 53.81; H, 4.04; N, 6.28%.

*7-(4'-Carbomethoxy-6'-laevo-menthoxyacetamino-2'-nitrophenoxy)metameconine (IX)*

The amino compound IVb (0.539 g), laevo-menthoxyacetyl chloride (0.31 g),  $[\alpha]_D = -85.75^\circ$  (c, 2.13 in chloroform) (25), and chloroform (30 ml) were heated under reflux for 6 hours. The crystals (0.1 g) which separated from the cooled solution had a m.p. of 228-232° (k), undepressed by admixture with authentic IVb. Evaporation of the mother liquors and trituration of the oily residue with petroleum ether gave a solid, which was sensitive to light, in a yield of 0.7 g, m.p. 183°. Five successive recrystallizations gave products of the following melting points (k): (from ethanol) 185-190°; (from ethanol) 188-191°; (from methanol) 188-190°; (from benzene - petroleum ether) 188-190°; (from ethanol) 188-189°; thus there was no evidence for the presence of stable diastereoisomers. Stout white needles. Found: C, 60.23; H, 6.08; N, 4.85%. Calc. for  $C_{30}H_{46}O_1N_2$ : C, 60.00; H, 6.00; N, 4.67%.

A solution of the menthoxy-amide (IX) (0.1467 g) in chloroform (solution volume 5 ml) was observed in the polarimeter; nine readings were taken over the period from 5 minutes to 68 hours after the formation of the solution, each reading, as well as the instrument's zero-point, being the mean of 10 observations. The corrected readings varied smoothly from the initial value of  $-0.85^\circ$  to the final value of  $-0.89^\circ$ ; the variation was probably not significant. The initial value gives  $[\alpha]_D = -29^\circ$  and a molar rotation of  $-174^\circ$ ; under approximately the same conditions the molar rotation of purified menthoxyacetic acid was found to be  $-190^\circ$ . The lack of mutarotation, and the approximate agreement of the molar rotations, were regarded as significant.

*Methyl 2-(4'-Carbomethoxy-2',6'-dinitrophenoxy)benzoate (VIA)*

Methyl 4-chloro-3,5-dinitrobenzoate (2.6 g) and dry pyridine (15 ml) were heated

5 minutes on the steam bath. Methyl salicylate (1.5 ml) was then added and the heating continued for 90 minutes. The dark colored solution deposited a bright yellow gum on being poured onto ice (100 g); when the gum had solidified it was recovered, washed with water, and dried. The crude mixed product was separated into its components in any of three ways.

(a) Recrystallization from acetonitrile gave bright yellow needles, m.p. 241–242° (uncorr.) in a yield of 0.4 g, or 11%. Evaporation of the mother liquors followed by recrystallization of the residue from ethanol gave the diphenyl ether VIa, m.p. 109.5–110.5°, yield 2.1 g (56%). One more recrystallization from ethanol gave the analytical sample, m.p. 110.6–111.2°. Found: C, 51.12; H, 3.50; N, 7.71%. Calc. for  $C_{16}H_{12}O_2N_2$ : C, 51.06; H, 3.22; N, 7.45%.

(b) Extraction with hot ethanol left the yellow needles undissolved; the ether was recovered by dilution of the ethanol. Further recrystallizations gave the same two products as before.

(c) The crude product was washed with dilute hydrochloric acid (which decomposed the yellow needles) and then recrystallized twice from ethanol to give the pure ether, m.p. 110–111°. On a larger scale, 23.3 g (73% of theory) of the twice recrystallized ether VIa, m.p. 110–111°, was made in this more convenient way.

The yellow needles are shown below to be N-(4-carbomethoxy-2,6-dinitrophenyl)-pyridinium 4'-carbomethoxy-2',6'-dinitrophenoxide (Ib).

*Stability of Methyl 2-(4'-Carbomethoxy-2',6'-dinitrophenoxy)benzoate (VIa) in Pyridine*

The dinitroether VIa (0.5 g) and dry pyridine (5 ml) were heated on the steam bath for 30 minutes, poured onto ice, the precipitate recovered and recrystallized from methanol. The product (0.4 g) had m.p. 111°, undepressed by admixture with the original ether. Hence the quaternary salt (Ib) did not arise from nucleophilic attack upon the diphenyl ether.

*Scissions of the Diphenyl Ether Linkage; Preparation of Methyl 2-(4'-Carboxy-2',6'-dinitrophenoxy)benzoate (VIb)*

(a) *With Hot Potassium Hydroxide*

The dimethyl ester VIa (0.3 g) was heated under gentle reflux for 30 minutes with 10% aqueous potassium hydroxide solution. The cooled, acidified solution deposited white crystals, m.p. 254–255° (uncorr.). Analyses were approximately correct for 3,5-dinitro-4-hydroxybenzoic acid (IIb), and the identification was confirmed by mixture melting point with authentic material (made by saponification of the methyl ester IIa, and twice recrystallized from ethanol; the melting point of 254–255° (uncorr.) was considerably higher than that (244–246°) observed by Christianson) (26).

(b) *With Cold Potassium Hydroxide*

The dimethyl ester VIa (3.0 g) was dissolved in hot ethanol and the solution rapidly cooled to give a suspension of very fine crystals. Potassium hydroxide solution (18 ml of 10%) was slowly added and the mixture shaken at room temperature for 5 minutes. Ether (50 ml) was then added, and the mixture acidified, separated, and the aqueous layer extracted with three 50-ml portions of ether. Exhaustive back extraction of the combined ethereal layers with cold sodium bicarbonate solution (each extract being rapidly chilled and acidified after the extraction) followed by re-extraction with ether of the acidified sodium bicarbonate extracts, and evaporation of the final, dried, ethereal extracts, gave a pale yellow oil containing some crystals. Recrystallization of the oily mixture from methanol gave 1.1 g of light-sensitive crystals m.p. 175–185°. Three more

wasteful recrystallizations from methanol gave the analytical sample of 2-(4'-carboxy-2',6'-dinitrophenoxy)benzoate, m.p. 214-215° (k). Found: C, 49.81; H, 2.90; N, 7.62%. Calc. for  $C_{15}H_{18}O_9N_2$ : C, 49.72; H, 2.76; N, 7.74%.

When a similar preparation was acidified after the reaction had proceeded for only 1 minute at room temperature, a strong odor of methyl salicylate could be detected. This observation, together with the isolation of the free dinitro acid (IIb) in (a) part, and the rapid saponification observed in the less activated ether (Va) (see above), made it sufficiently clear that it was the less activated ester group which remained in compound VIb.

(c) *With Acids*

When the dimethyl ester VIa was heated under reflux with dilute acetic acid containing a little *p*-toluenesulphonic acid, it was recovered unchanged almost quantitatively. An attempted transesterification with glacial acetic acid and *p*-toluenesulphonic acid gave no detectable methyl acetate in the fractionating column, and again the recovery of unchanged material was almost quantitative. When concentrated sulphuric acid was allowed to react with the ester at room temperature for 14 hours, and the mixture poured into water, recovery of the starting material was lower, and a strong odor of methyl salicylate showed that some rupture of the ethereal linkage had occurred.

(d) *With Methoxide Ion*

The dimethyl ester VIa (2 g) was dissolved in a methanolic solution of barium hydroxide hydrate (64 ml of a solution containing 18 g of the hydrate per liter) and allowed to react for 3 minutes at room temperature. No precipitate formed. The deep red solution was then acidified, diluted with water, and extracted with ether. The ethereal extracts were dried and evaporated; the yellow oil remaining (1.7 g) had a strong odor of methyl salicylate. Extraction of an ethereal solution of the oil with aqueous sodium bicarbonate, removal of the ether, and recrystallization of the residue from methanol gave white crystals in a yield of 0.6 g, whose m.p. of 54-55° was not depressed by admixture with authentic methyl 3,5-dinitro-4-methoxybenzoate (IIc) (prepared by the action of diazomethane upon IIa, and recrystallized from methanol, m.p. 52-53°).

Methyl 3,5-dinitro-4-hydroxybenzoate (IIa) (1 g) was dissolved in 150 ml of the same solution of barium hydroxide hydrate in methanol, and allowed to stand 3 days at room temperature. The bright orange crystals (1.7 g) of the barium salt were recovered, suspended in water (150 ml), and acidified; the free acid slowly precipitated and on recovery it had a m.p. of 249-250° (uncorr.) undepressed by admixture with authentic IIb. Thus the scission of the ether had been accomplished by direct nucleophilic attack of methoxide, and not, for example, by hydrolysis followed by methylation of the free phenolic group by the activated methyl ester.

(e) *With Hydrazine*

The dimethyl ester VIa (1 g) was suspended in absolute alcohol and treated with a solution of hydrazine hydrate (0.4 g) in ethanol (2 ml). A little Raney nickel was added and the mixture heated under reflux for 1 hour, more ethanol being added to keep the product in solution. The hot solution was filtered from the Raney nickel and cooled; the red crystals (0.3 g) which separated were recovered and thrice recrystallized from ethanol to give thick red needles of 4-carbomethoxy-2,6-dinitrophenylhydrazine (VII), m.p. 171° (k). Found: C, 37.58; H, 3.26; N, 22.03%. Calc. for  $C_8H_8O_6N_4$ : C, 37.51; H, 3.12; N, 21.87%. The phenylhydrazine reacted with benzaldehyde to give a derivative which on purification consisted of orange plates, m.p. 241° (k), not further characterized.

*Methyl 2-(6'-Amino-4'-carbomethoxy-2'-nitrophenoxy)benzoate (VIc)*

The dinitro ester VIa (1 g) was dissolved in glacial acetic acid (25 ml) and gently warmed to 30° with iron powder (0.45 g). The temperature then rose spontaneously to 55° and was kept at 50–55° for 15 minutes by external cooling. Allowed to cool by itself during 30 minutes more, the mixture was then filtered from a precipitate which was washed with hot glacial acetic acid. The combined filtrates were evaporated to dryness, the residue thoroughly extracted with ether, the ether evaporated, and the residual oil recrystallized from methanol with charcoal to give 0.5 g of yellow crystals, m.p. 134–138°. Five successive recrystallizations from methanol gave crystals of grossly erratic shape and melting point. In a second preparation, the product was recrystallized once from methanol and then five times from benzene, with the same erratic results (which were therefore not due to solvent of crystallization) (see below). The final analytical sample so obtained consisted of needles, m.p. 135° (k). Found: N, 8.16%; and on another sample: C, 55.67, 55.63%; H, 4.08, 3.92%. Calc. for  $C_{16}H_{14}O_7N_2$ : C, 55.49; H, 4.08; N, 8.09%.

*Dimorphism of Methyl 2-(6'-Amino-4'-carbomethoxy-2'-nitrophenoxy)benzoate (VIc)*

The analytical sample of the amino ester VIc (0.2 g, m.p. 139°) was heated at 150° for 45 minutes to give a clear yellow melt without any signs of decomposition. Allowed to cool slowly, the melt produced crystals of m.p. 141–143°; admixture with the starting material gave an intermediate m.p. of 137–139°. Recrystallization of the solidified material from methanol gave a mixture of crystals of two distinct forms: (a) pale yellow "prisms" (b) slightly darker yellow "plates". The two forms were separated by hand, and careful examination of the prisms (type "a") under the microscope showed them to be perfectly free from crystals of type "b". Nevertheless, recrystallization of the prisms from methanol gave plates of type "b". Careful heating of these plates on the hot stage of the microscope showed melting to begin at 135°; at 137° crystals of the prism type "a" appeared in the melt, and at 139° the sample had solidified entirely into the prism form, which then melted at 144–145°. This sequence, remarkable for its reproducibility, has twice been recorded photomicrographically by Professor J. R. Allen, as shown in Plate I.

Infrared spectra of the solid plates and prisms in potassium bromide disks showed differences in the regions of 1300 to 1375  $\text{cm}^{-1}$ , and 3280 to 3300  $\text{cm}^{-1}$ , but the infrared spectra of chloroform solutions of the two forms were identical.

*Methyl 2-(6'-Acetamino-4'-carbomethoxy-2'-nitrophenoxy)benzoate (VID)*

The amino ester VIc (0.1 g, m.p. 142°), acetic anhydride (1 ml), and concentrated sulphuric acid (1 drop) were heated together to complete solution, then diluted with water (20 ml) and heated to destroy the acetic anhydride. When cool, the solution deposited pale yellow needles which after four recrystallizations from aqueous ethanol gave the colorless analytical sample m.p. 149–150° (k). Found: C, 55.43, 55.29; H, 4.19, 4.29; N, 7.75%; and on another sample: N, 7.14, 7.35%. Calc. for  $C_{18}H_{16}O_8N_2$ : C, 55.68; H, 4.12; N, 7.22%.

*8-Carbomethoxy-6-nitro-11-oxo-10,11-dihydro-dibenz[b,f][1,4]oxazepine (Lactam of 2-(6'-Amino-4'-carbomethoxy-2'-nitrophenoxy)benzoic Acid (VIII)*

(a) The amino ester VIc (0.2 g, m.p. 135°) was heated in an oil bath at 210° for 30 minutes. Decomposition was evident, and the cooled melt was a black tar coated with white crystals. Extraction with hot methanol left the white crystals as an insoluble residue, m.p. 315–316° (k).

(b) The dinitro ester VIa (0.5 g), dissolved in glacial acetic acid (15 ml), was heated for

30 minutes on the steam bath with a solution of stannous chloride dihydrate (1.0 g) in concentrated hydrochloric acid (2 ml). White needles were recovered from the cooled reaction mixture; one recrystallization from glacial acetic acid gave 0.1 g of fluffy needles, m.p. 289–291° (uncorr.), and two more similar recrystallizations gave the analytical sample, m.p. 315–316° (k). Found: C, 57.75; H, 3.59; N, 8.83%. Calc. for  $C_{15}H_{10}O_6N_2$ : C, 57.32; H, 3.19; N, 8.92%. The melting point was not depressed by admixture with the product from (a), and the infrared spectra of the two preparations were identical.

*Supposed N-(4'-Carbomethoxy-2',6'-dinitrophenyl)pyridinium Chloride (Ia)*

Methyl 4-chloro-3,5-dinitrobenzoate (2.6 g) (15) in dry benzene (20 ml) was treated with dry pyridine (1.5 ml). After 1 hour the slightly sticky yellow crystals were recovered, washed with benzene and then with acetone, dissolved in warm ethanol, and reprecipitated with ether to give white prisms (3.0 g, 88%), m.p. 117–120°. Since they decomposed very rapidly indeed they were characterized indirectly as described below.

*N-(4-Carbomethoxy-2,6-dinitrophenyl)pyridinium 4'-Carbomethoxy-2',6'-dinitrophenoxide (Ib)*

(a) The pyridinium chloride Ia (3.4 g) was dissolved in water (10 ml) and shaken with silver oxide (freshly prepared from 3.4 g of silver nitrate). Filtered from the silver compounds, the solution was slowly added to a suspension of methyl 3,5-dinitro-4-hydroxybenzoate (IIa) (27) (2.5 g) in boiling water (150 ml). The bright yellow precipitate was recovered, washed with water, and then with acetone (100 ml) to remove unchanged phenol. The initial melting point of 236–237° (decomp.) was raised to 242–243° (k) (decomp.) by two recrystallizations from acetone. Found: C, 46.67, 46.52; H, 2.72, 2.77%. Calc. for  $C_{21}H_{16}O_{13}N_4$ : C, 46.25; H, 2.77; N, 12.84%.

(b) The yellow needles, m.p. 240–242° (uncorr.), obtained as a by-product in the preparation of IVa as described above were the same substance as that obtained in (a) part (mixture melting point, identical infrared spectra). Found: C, 47.90; H, 2.89; N, 12.88%. The presence of the activated N-phenylpyridinium group was shown by the slow solubility of the crystals in cold dilute potassium hydroxide to give a deep red coloration (20)—a test not given by the diphenyl ethers or dinitrohydroxybenzoic acids of this series. When this preparation of the quaternary salt (0.35 g) was heated for 3 hours on the steam bath with dry pyridine (3 ml) and the mixture poured onto ice, the solid recovered and recrystallized from acetone, unchanged quaternary salt was obtained in a yield of 0.2 g, m.p. 240–242° (uncorr.). Thus the salt is resistant to hydrolysis and to transformation into a diphenyl ether (19).

(c) The yellow needles, m.p. 241–242°, isolated from the preparation of VIa as above were also identical with those from (a) and (b) (mixture melting point, infrared spectra). Another sample of the yellow needles from the same source was recrystallized four times from acetonitrile and twice from acetone. Found: C, 46.18, 46.18; H, 2.30, 2.25; N, 12.98, 12.85%. Allowed to stand in the cold with dilute potassium hydroxide solution, the crystals slowly gave the deep red color characteristic of activated N-phenylpyridinium compounds.

Further proof of identity and structure is given in the next section.

*Decomposition of the Quaternary Salt Ib*

(a) A sample of the quaternary salt Ib (3.0 g, prepared as in "a" above) was stirred 5 minutes with dilute hydrochloric acid. The deep yellow color of the phenoxide was slowly replaced by the cream color of the insoluble decomposition product. This precipitate on recovery was shown to be methyl 3,5-dinitro-4-hydroxybenzoate (IIa) by melting point and mixture melting point—a demonstration of the anion of the quaternary salt.

The aqueous filtrates after being neutralized with sodium bicarbonate gradually deposited a yellow solid which was recovered next morning, yield 0.88 g. Four recrystallizations from acetone converted it to long pale yellow needles, m.p. 244–245° (uncorr.) (decomp.).

(b) A sample of *Ib*, recovered from the preparation of *IVa*, and as described in part (b) of the previous section, gave the same results. In particular, the precipitate from the neutralized solution had the same infrared spectrum as that described in part (a) of this section. Thus the identity of the two specimens of *Ib* had been demonstrated.

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## GUANIDINE COMPOUNDS

### III. THE PREPARATION OF TRIACETYLGUANIDINE AND ITS TRANSFORMATION WITH ALCOHOL<sup>1,2</sup>

R. GREENHALGH AND R. A. B. BANNARD

#### ABSTRACT

Triacetylguanidine has been prepared and shown to undergo stepwise deacetylation in the presence of alcohol to guanidine acetate. Diacetylguanidine has been shown to have a m.p. 176–177° and not 166° as previously reported.

Acetylation of guanidine under mild conditions gave a compound m.p. 110–112°, in 82% yield, which had not previously been reported by Korndorfer (1), Grundmann and Beyer (2), Ryabinin (3), or Cockburn and Bannard (4). The substance could be purified by crystallization from acetone or sublimation *in vacuo*. Its ultraviolet spectrum differed from those of model diacetyl- and monoacetyl-guanidine derivatives. The diacetylguanidines showed two bands in the regions 222–229 m $\mu$  and 255–265 m $\mu$ , and the monoacetylguanidines only one band at 230–236 m $\mu$  (5). Analytical data gave an empirical formula C<sub>7</sub>H<sub>11</sub>O<sub>3</sub>N<sub>2</sub>, which together with acetyl and molecular weight determinations showed the compound to be triacetylguanidine.

The most important property of triacetylguanidine is its instability in the presence of hot alcohol. Treatment with ethanol at 75° for 30 minutes or repeated recrystallization from methanol gave a compound, m.p. 176–177°, which sublimed unchanged *in vacuo*. This compound was shown to be different from monoacetylguanidine acetate (m.p. 178–180°), since admixture with an authentic sample depressed the melting point, also the infrared spectra of the two compounds differed. No free acetic acid was present, as indicated by the fact that no sodium hydroxide was consumed on potentiometric titration. The ultraviolet spectrum indicated a diacetylguanidine and the analytical data agreed with this. Confirmation was obtained by the preparation of a picrate m.p. 162–164°, which analyzed for diacetylguanidine picrate. Previously, Ryabinin (3) had obtained a substance, m.p. 166°, which he designated as diacetylguanidine and which gave a picrate, m.p. 162–164°. Since we could also isolate the compound, m.p. 176–177°, by following Ryabinin's procedure for acetylation of guanidine, we concluded his sample was impure. A possible explanation for the failure of previous workers to isolate the triacetyl derivative could be their use of more vigorous conditions. Treatment of triacetylguanidine with acetic acid led to a number of unstable intermediates, which on drying *in vacuo* gave the diacetyl derivative. The acetic acid formed during acetylation under these vigorous conditions could be expected to yield these intermediates, which on drying as Ryabinin did, would give diacetylguanidine.

When diacetylguanidine was treated with ethanol under conditions similar to those used with triacetylguanidine a compound, m.p. 187–189°, was obtained which was shown to be identical with monoacetylguanidine. Monoacetylguanidine in its turn when treated with ethanol gave guanidine acetate. Thus we were able to deacetylate triacetylguanidine

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to guanidine acetate in a stepwise manner, each step proceeding with a yield greater than 55%. In acidic methanol, deacetylation occurs even more readily, as can be shown by treatment of diacetylguanidine in methanol with 1 equivalent of acetic acid, when monoacetylguanidine acetate is formed almost instantaneously. On substituting N,N-dimethylformamide for methanol as solvent no deacetylation occurs, although monoacetylguanidine is readily converted to the acetate salt in the presence of 1 equivalent of acetic acid.

No attempt was made to study the kinetics of the stepwise deacetylation, but the high yields obtained would suggest that it is not a simple first-order sequential reaction.

#### EXPERIMENTAL\*

##### *Triacetylguanidine*

Guanidine acetate (500 mg) was heated for 1 hour on the steam bath with acetic anhydride (5 ml). The solution was taken to dryness *in vacuo* yielding a colorless oil which slowly crystallized. Recrystallization from acetone gave 636 mg (82%) of colorless thick needles, m.p. 110–112°. Calc. for  $C_7H_{11}O_3N_3$ : C, 45.40; H, 5.99; N, 22.69;  $CH_3CO$ , 69.7%; mol. wt., 184. Found: C, 45.47; H, 5.86; N, 22.94;  $CH_3CO$ , 68.65%; mol. wt., 182. The compound could also be purified by sublimation *in vacuo* (70–80° at 0.005 mm). Ultraviolet spectrum in ethanol,  $\lambda_{max}$  214 m $\mu$ ,  $\epsilon_{max}$  15,260;  $\lambda_{max}$  250 m $\mu$ ,  $\epsilon_{max}$  9712: (concn. 0.8 mg/100 ml).

##### *Conversion of Triacetylguanidine to Diacetylguanidine*

Triacetylguanidine (503 mg) was dissolved in ethanol (1.0 ml) and heated for 30 minutes at 75°. When the solution was concentrated, colorless prisms separated. They were recrystallized from methanol–ether, yielding 275 mg (71%) of diacetylguanidine, m.p. 176–177°. Calc. for  $C_6H_9O_2N_3$ : C, 41.95; H, 6.34; N, 29.36;  $CH_3CO$ , 60.15%. Found: C, 41.86; H, 6.33; N, 29.51;  $CH_3CO$ , 58.7%. On admixture with an authentic sample of monoacetylguanidine acetate, m.p. 178–180°, the melting point was depressed to 164°. Diacetylguanidine sublimed unchanged at 105–110° at 0.005 mm. Ultraviolet spectrum in ethanol  $\lambda_{max}$  212 m $\mu$ ,  $\epsilon_{max}$  8921;  $\lambda_{max}$  248 m $\mu$ ,  $\epsilon_{max}$  16,840: (concn. 1.09 mg/100 ml). The picrate was prepared by adding the theoretical amount of picric acid in methanol to diacetylguanidine in methanol, m.p. 162–164°. Calc. for  $C_{11}H_{12}O_9N_6$ : C, 35.49; H, 3.25; N, 22.58%. Found: C, 35.73; H, 3.19; N, 22.05%.

##### *Conversion of Diacetylguanidine to Monoacetylguanidine*

Diacetylguanidine (250 mg) was treated with ethanol as above. The colorless prisms obtained were recrystallized from methanol–ether, m.p. 188–190°, yield, 103 mg (55%). Identified by mixed melting point and infrared spectrum as monoacetylguanidine.

##### *Conversion of Monoacetylguanidine to Guanidine Acetate*

Monoacetylguanidine (250 mg) was treated with ethanol as above. Recrystallization of the crude product from methanol–ether gave 187 mg (74%) of colorless prisms, m.p. 227–229°. Identified by infrared spectrum and no depression of melting point on admixture with a sample of guanidine acetate.

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\*All melting points are corrected.

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# AN ELECTRON DIFFRACTION STUDY OF ELECTROPOLISHED IRON<sup>1</sup>

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## ABSTRACT

Iron has been electropolished over a range of voltage and current in the acetic acid-perchloric acid bath. Under optimum conditions an "atomically smooth" surface has been obtained as evidenced by marked refraction effects in the electron diffraction patterns. There is also evidence for a thin film on the electropolished surface which thickens on further exposure to air to form a preferentially oriented cubic iron oxide. Light etching in nitric acid removed the film and formed a surface which, on diffraction, gave the more normal spot pattern of iron.

## INTRODUCTION

The behavior of metals in corrosion and oxidation studies is very dependent on the original method of surface preparation. Mechanical polishing leads to plastic deformation of the structure which may penetrate quite deeply into the metal. Some impurities and original oxide film may be introduced into the metal by the polishing agent. Subsequent etching to remove the deformed layer can lead to surfaces with high and variable surface roughness factors. Hydrogen reduction may introduce hydrogen into the metal and roughen the surface. For these reasons there has been a great deal of interest in the use of electropolishing as a method of surface preparation.

Satisfactory electropolishing gives rise to an undulating surface which may best be described as "atomically smooth" (1). During reflection electron diffraction examination, the incident electron beam enters such a surface at varying angles of grazing incidence. Each resulting diffraction image is thus built up of a series of diffracted beams suffering slightly different refraction displacements towards the shadow edge. The over-all effect is the elongated spot pattern commonly found with electropolished surfaces (2).

Pashley (1) indicates that on a flat substrate uniform films of the order of 2 Å thick (monolayers) may be detected by electron diffraction under favorable conditions. Available information suggests that a layer of material 25–50 Å thick completely obscures the low angle diffraction maxima of a flat substrate (3, 4, 5). It follows that marked refraction streaking of the substrate pattern and low background scatter strongly suggest freedom from such extensive contamination.

There have been a number of attempts to produce "clean" and smooth iron surfaces by electropolishing. Recently Ladage (6) has reported the satisfactory electropolishing of iron in an ortho-phosphoric–chromic acid bath. Boswell (7) has electropolished iron in a chromic–acetic acid bath. Both these baths may contaminate the surface with chromium or phosphorus compounds.

Electropolishing polycrystalline iron in the perchloric–acetic anhydride bath (8), Cohen (9) obtained surface films which obscured the substrate. Iron surfaces polished in a bath of different composition (10) were also contaminated by a film estimated to be about 100 Å thick by electron microscopy. Wilman *et al.* (11, 12, 13) have polished iron single crystals in the perchloric–acetic anhydride bath (8) and claim to have produced clean "atomically smooth" surfaces. The somewhat restricted spot elongation that is

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apparent in their published patterns and the absence of diffuse spots from an air-formed film suggest that much of their surface was etched.

The present paper describes a procedure for preparing an iron surface by electro-polishing which, as evidenced by electron diffraction, is a closer approximation to a clean "atomically smooth" condition than has heretofore been achieved.

#### EXPERIMENTAL

A Ferrovac iron (Al 0.0005%, C 0.007%, Cr 0.002%, Mn 0.0002%, Ni 0.0009%, Si 0.002%, S 0.0015%) sheet, 10 mil in thickness, cut into  $1.5 \times 5.0$ -cm coupons with a 2.5-cm  $\times$  2-mm tail was used. As received, this iron contained excessive oxide inclusions, which rendered optical judgment of electropolishing impossible. To remove this oxide, several Ferrovac coupons, mechanically polished down to 4/0's were reduced for 99 hours in wet hydrogen followed by a further 84 hours in dry hydrogen continuously above  $1100^\circ$  C.

Metallographic examination of this iron showed that the oxide inclusions had been largely removed. The slow cooling after the high-temperature treatment led to sufficient grain growth in the polycrystalline sheet to allow diffraction patterns to be obtained from single grains.

The internally clean iron polycrystals were electropolished in a 20/1 glacial acetic acid/70% perchloric acid solution under an optimum bath potential of  $105 \pm 5$  volts d-c. (ripple  $\geq 300$  millivolts). This bath was chosen since the iron surfaces were required for corrosion studies in the absence of avoidable contaminants. Thus complete removal of a perchlorateacetate anolyte is more likely than a chromium, phosphate, or sulphate anolyte. The "areal average" current density was  $0.4-0.5 \text{ \AA/cm}^2$  under proper conditions of stirring in the bath geometry illustrated in Fig. 1. With an initial bath temperature of  $17 \pm 2^\circ$  C each coupon was polished for a total period of 3 minutes in 10-second bursts.

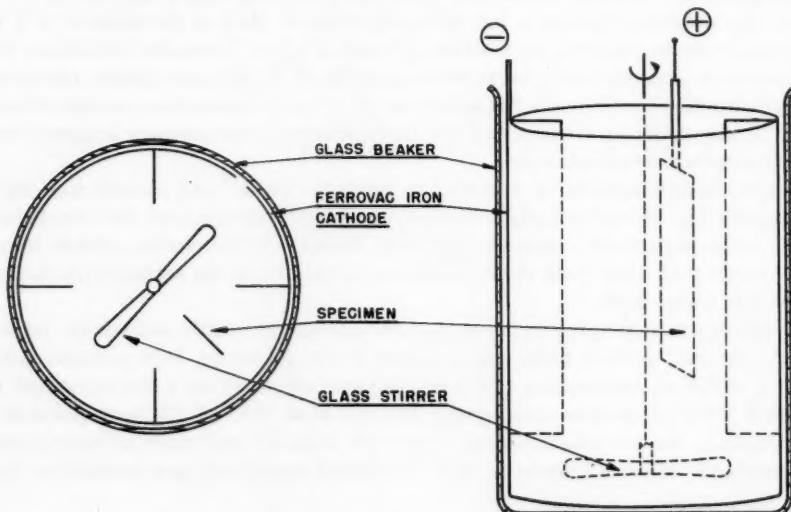


FIG. 1. Schematic diagram of electropolishing cell.

Each 10-second treatment resulted in the removal of iron to a depth of  $1.2 \mu$ . While waiting for the bath to cool, we washed the coupon in a jet of anhydrous redistilled

methyl alcohol and held it inverted. On removal from the final 10- to 15-second electro-polish (which was also found to be a sufficient period to eradicate the effects of the subsequent etching employed), the coupon was withdrawn from the bath under potential and washed generously (200 ml) and immediately in a jet of anhydrous methyl alcohol.

At 1000-diameter magnification such coupon surfaces were optically featureless save for sharp steps at the few grain boundaries. These steps, initially present on the iron after reduction, were not removed by prolonged electropolishing.

A number of polishing variables were investigated. The best results were obtained by polishing in fresh solutions. Such coupon surfaces gave the most marked refraction elongation in diffraction patterns and the best optical polish. Coupons polished in solutions which had been used repeatedly gave some degree of refraction elongation until the solution took on a brown coloration. The presence of ferric ion was suspected of having deleterious effects.

Optimum stirring conditions were determined by trial and error. Inadequate agitation of the bath by stirring gave rise to local etching even at optimum polishing conditions, while excessive agitation disrupted the anolyte layer causing irregular polishing.

A cell voltage of less than 100, for example, 80 volts, produced plateaux with flower-like peripheries on an otherwise well-polished surface. Electron diffraction showed relatively weak iron spots with a high background, which indicated a contaminated surface. At cell voltages of greater than 110, for example, 120 volts, a smooth clean surface with microetching just visible at 1000 diameters was obtained and little evidence of refraction elongation of the diffraction spots was observed.

The removal of the coupon with or without disconnecting the applied potential appeared to make no difference provided the anolyte was displaced quickly. Allowing the anolyte to disperse in the polishing solution caused the surface to pick up excess contamination, as evidenced by a higher ratio of background scatter to spot intensity. In contrast, leaving the anolyte on the iron surface after removal from the bath caused sufficient etching within 60 seconds to obliterate refraction elongation of the diffraction spots.

After final rinsing in alcohol the coupons were transferred under methyl alcohol to the specimen chamber of the electron diffraction camera. In subsequent etching experiments the coupon was agitated under 0.05% nitric acid in conductivity grade water, washed generously with an alcohol jet, and returned to the camera while still moist.

All electron diffraction photographs were taken using a camera length of 50 cm and an accelerating voltage of 50 kilovolts.

## RESULTS

The results shown are typical of those obtained from large crystals which developed in the coupons during annealing. The crystal chosen for study had a (521) plane almost parallel to the macroscopic surface, and the diffraction pattern observed with the electron beam parallel to the [113] zone axis is indexed in Fig. 2. The specimen was bent slightly to allow the electron beam to be incident on the surface of this particular crystal. The resulting lattice distortion prevented the formation of sharp Kikuchi lines. Many orders of reflection were observed at the one setting of angle of incidence.

On electropolishing this specimen under optimum polishing conditions, Fig. 3 was obtained. Figure 3 shows marked refraction elongation of all spots towards the shadow edge, characteristic of an "atomically smooth" surface. A diffuse spot not belonging to the iron pattern is visible below the (220) iron reflection in Fig. 3. This is attributed to an overgrowth film which also contributed to the background scatter. After a 15-second etch

in 0.05% nitric acid, the diffuse background was reduced and the iron pattern increased in intensity (Fig. 4). A diffuse spot still appearing below the (220) iron reflection indicates that some oriented overgrowth was again present on the surface. Little change in the spot elongation suggests that most of the substrate metal was unaffected. (Double spots appearing in Figs. 4, 5, and 6 occurred as a result of the unintentional location of a second crystal of similar orientation in the incident beam.) Figures 5 to 8 illustrate the effect of further etching. Refraction elongation of the iron reflections was gradually reduced and the intensity of the spot from the overgrowth diminished. The diffraction spots in Fig. 8 are characteristic of an etched surface where diffraction is a result of transmission through etch structures.

Exposure of an electropolished surface to the atmosphere at 20° C for 17 hours resulted in Fig. 9. The intensity of the overgrowth spot below the (220) iron reflection has greatly increased and numerous other diffuse reflections are visible.

## DISCUSSION

### (1) Diffraction Pattern from Substrate

The details of refraction phenomena in electron diffraction have been discussed by a number of authors (14, 15). Relationships between the angle of incidence of the electron beam ( $\phi$ ), the Bragg angle of reflection within the crystal ( $\theta$ ), and the inner potential of the specimen ( $\Phi$ ) are developed in the above literature. A discussion of refraction effects on electropolished surfaces has recently been published (16). The gradual change of refraction elongation of the iron reflections may be discussed with reference to the idealized models in Fig. 10.

On an atomically flat surface (Fig. 10(a)), the electron beam suffers refraction as it enters and leaves the crystal through the same surface plane  $SS'$  by the path  $ABCDE$ . It may be shown to suffer an angular displacement of  $2(\theta - \phi)$  from the direction of the electron beam in the absence of refraction  $FBCDG$ . For metal crystals, the inner potential giving rise to this refraction effect is generally of the order of 10 to 15 volts positive. The resulting angular displacement of the electron beam may be about 0.017 radian for low orders of reflection and grazing angles of incidence. If the distance between the specimen and the photographic plate in the diffraction apparatus is 50 cm, the displacement is recorded as an 8.5-mm shift of the diffraction spot towards the shadow edge of the photograph. Some symmetrical spot broadening may be expected due to lack of penetration of the beam normal to the surface of the specimen, resulting in diffraction spots of the type illustrated in Fig. 10(a). Such discrete spot displacements are observed on cleavage faces of many crystals and are clearly demonstrated by cleaved rock-salt surfaces (17).

Should isolated etch pits develop on an atomically flat surface, the path of the electron beam may be that of  $ABCDE$  shown in Fig. 10(b). When the facet  $S'S''$  makes an angle  $\beta$  greater than about 10° with the surface plane  $SS'$ , the deviation of the beam  $CDE$  passing across the surface  $S'S''$  is negligible. Under such conditions the angular displacement of the beam from the direction in the absence of refraction ( $FBCDE$ ) is  $(\theta - \phi)$ . If the angle  $\beta$  has values between 0 and 10° the beam suffers refraction displacements varying between  $2(\theta - \phi)$  and  $(\theta - \phi)$ .

A more markedly etched surface may be composed entirely of structures of the type Fig. 10(c). The electron beam will suffer no apparent change in direction on passing across the facets  $SS'$  or  $S''S'''$  providing the angles  $\beta$  and  $\beta'$  are greater than about 10°. If the facets  $S'S''$ , parallel to the surface, are not developed, all refraction effects should

PLATE I

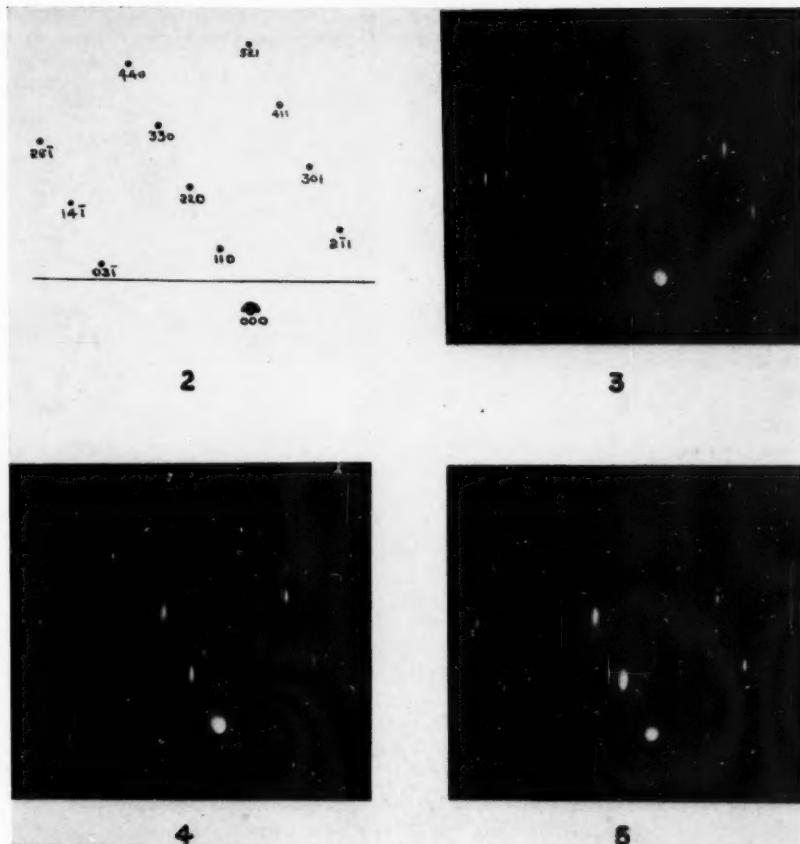


FIG. 2. Indexed diffraction pattern from iron surface almost parallel to (521) plane. Electron beam parallel to  $\langle\bar{1}13\rangle$  zone axis.

FIG. 3. Electron diffraction pattern of freshly electropolished surface.

FIG. 4. As Fig. 3 plus 15-second etch in 0.05% nitric acid.

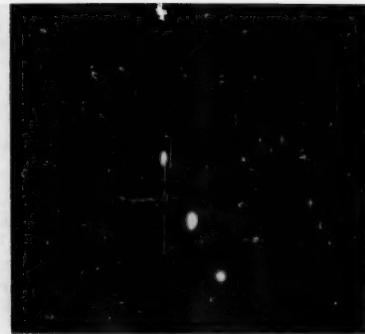
FIG. 5. As Fig. 4 plus 15-second etch in 0.05% nitric acid.

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PLATE II



6



7



8



9

FIG. 6. As Fig. 5 plus 15-second etch in 0.05% nitric acid.

FIG. 7. As Fig. 6 plus 15-second etch in 0.05% nitric acid.

FIG. 8. As Fig. 7 plus 30-second etch (total 90-second etch).

FIG. 9. Diffraction pattern of electropolished specimen after exposure to dry air at room temperature for 17 hours.

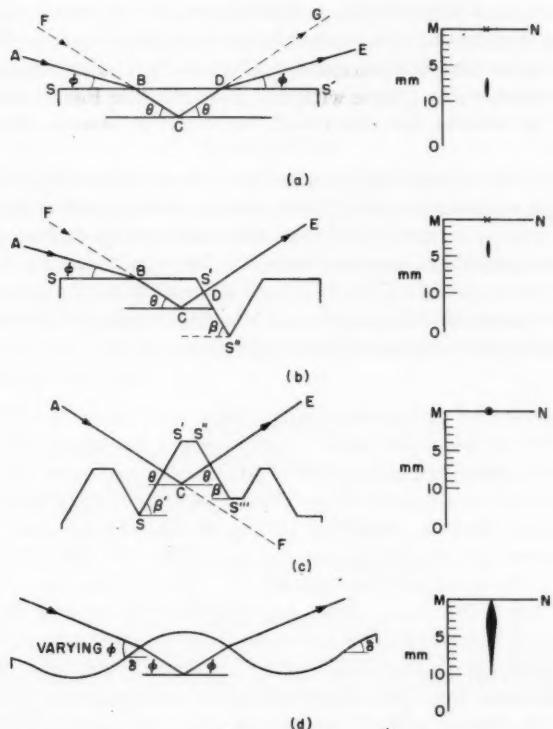


FIG. 10. Idealized models of specimen surfaces showing path of electron beam. Corresponding spot shape is illustrated. Reference line  $MN$  shows spot position in absence of refraction. Direction  $MO$  represents refraction displacement towards the shadow edge.

(a) Atomically flat surface; (b) very lightly etched flat surface; (c) heavily etched surface; (d) slightly rolling surface characteristic of electropolishing.

be absent. Small circular diffraction spots should appear in the positions calculated from the normal Bragg relationship ( $n\lambda = 2d \sin \theta$ ). The beam suffers a deviation of  $2\theta$  from the initial direction  $ACF$  (Fig. 10(c)).

The current concept of an electropolished or "atomically smooth" surface is illustrated in Fig. 10(d). The rolling nature of this surface gives rise to a range of angles of incidence ( $\phi$ ), which when considered in conjunction with a mosaic structure in the crystal, results in elongated diffraction spots of the type illustrated. The displacement of the region of maximum intensity in the spot from the normal Bragg position has been shown to be a function of the mean angle of slope ( $\delta$ ) of the rolling surface, the inner potential of the crystal, and the electron-accelerating voltage (16).

This explanation of refraction elongation of spots from electropolished surfaces is found to be at fault when considered in detail. The concept of a smooth rolling structure on a surface parallel to a major crystallographic plane becomes questionable when the mean angle of slope ( $\delta$ ) is of the order of 0 to  $10^\circ$ . These problems will be discussed more fully in a note to be published elsewhere.

For the present, an "atomically smooth" surface (Fig. 10(d)) would account for the shape of the diffraction spots observed from the electropolished surface of an iron single

crystal (Figs. 3 and 4). With etching, pits developing in the metal enable effects of the type Fig. 10(b) to contribute more strongly to the spot intensity. The observed spot elongation due to refraction is thus reduced (Figs. 5, 6, 7). Further etching covers the surface with structures of the type Fig. 10(c). If a suitable etchant is chosen so that no facets parallel to the surface are developed, no evidence of spot elongation should be apparent (Fig. 8).

At present it is not possible to determine from the shape of the diffraction spots the relative areas of the specimen surface giving rise to the separate effects Figs. 10(a), (b), (c), and (d). The change in spot elongation observed during etching serves only as an indication that intermediate states exist between that of an electropolished (Fig. 10(d)) and the completely etched state (Fig. 10(c)). It is hoped that the correlation of electron micrographs and electron diffraction photographs from such surfaces will enable a more accurate assessment of the surface microstructure.

### (2) Overgrowth

The overgrowth material giving rise to the diffuse spot below the (220) iron reflection in Fig. 3 is probably an oxide film formed during electropolishing. The identification of this material is being attempted using similar results obtained from iron surfaces parallel to other crystal planes. On exposure of an electropolished surface to air for 17 hours at 20° C, the overgrowth thickens, resulting in Fig. 9. The diffuse spots due to the overgrowth in this pattern are in good agreement with either of the cubic oxides  $Fe_3O_4$  or  $\gamma-Fe_2O_3$ , confirming the results of Nelson (18) and Haase (19). The (111) plane of the oxide is parallel to the (110) of the metal, and the [112] azimuth of the oxide is parallel to the [113] azimuth in the metal. This corresponds to an orientation of the close-packed oxygen planes in the oxide on the closest-packed (110) planes in the b.c.c. iron. A more complete investigation of this epitaxial relationship is in progress. Figure 9 illustrates the suitability of the electropolished surface for the investigation of thin oxide films. Cathodic reduction of such an air-formed film of oxide on iron shows it to be of the order of 10 to 20 Å thick.

After etching of the electropolished surface, a diffuse spot is still visible below the (220) iron reflection (Figs. 4 to 8). This spot is due to an overgrowth material developed during rinsing and air exposure as the specimen was loaded into the diffraction apparatus and the instrument evacuated. The film should develop to the same thickness on each exposure after etching. The observed decrease in intensity of the spot due to this material in Figs. 4 to 8 resulted from the decreased ratio of film to substrate which was traversed by the electron beam on the etched surface.

### (3) Electropolishing

Electropolishing is generally considered to take place by the anodic dissolution of metal through a thin film of conversion product. During the process both metal and film dissolve. The composition of the film probably depends on both the current density and potential and is probably different from the film formed on air exposure. At voltages and current densities below the optimum there appears to be a thick polishing film which is uneven in thickness or conductivity and leads to both uneven polishing and high scattering of the electron beam. At higher than the optimum voltage and current density the polishing film is too thin to prevent etching of the metal by the highly acid polishing solution. Due to different activities of the different crystal planes some very light etching was occasionally observed on some grains even under good polishing conditions. This etching takes place first on grains with a (110) plane parallel to the specimen surface.

The strong refraction effect on the smooth electropolished surface results in broad banding in the electron diffraction patterns of randomly oriented polycrystalline specimens. It would appear that the assessment of electropolished surfaces by the use of electron diffraction should be made using large-grained polycrystals or single crystals.

#### CONCLUSION

Iron can be electropolished in the acetic-perchloric bath to give an "atomically smooth" surface with a very small amount of overgrowth. The film formed during electropolishing can be removed by treatment in dilute nitric acid. This treatment also etches the metal, thus changing the character of the diffraction pattern. On exposure to air, the film present after electropolishing thickens to form a cubic iron oxide with preferred orientation. On the basis of the electron diffraction evidence, the electropolishing and etching procedure developed above should serve as a proper method of specimen preparation for corrosion and oxidation studies.

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## OXIDATION OF D-GALACTURONIC ACID WITH SOME DELIGNIFYING AND BLEACHING AGENTS<sup>1</sup>

R. H. ZIENIUS<sup>2</sup> AND C. B. PURVES

### ABSTRACT

D-Galacturonic acid was oxidized with decreasing ease, and in the approximate order shown, by excess of the following agents: sodium chlorite near pH 2.8 and 75°; sodium hypochlorite at pH 10–11 and 25°; chlorine dioxide, pH 1.3 or 5 at 75°; chlorine near 0° and pH 5 (slight); and hydrogen peroxide at pH 10–11 and 25° (negligible). Some uronic acid was always recovered unchanged, even from conditions that would have oxidized glucose quantitatively to gluconic acid. The only other products were mucic acid, together with DL-tartaric acid and tartronic acid presumably derived therefrom. Chlorine dioxide, however, never produced tartronic acid. Methyl- $\alpha$ -D-galacturonoside methyl ester yielded some galacturonic acid when exposed to alkaline hypochlorite or peroxide, and this cleavage of the glycosidic group was tentatively attributed to the oxidants rather than to the alkalinity of the systems.

Anhydrous bromine degraded the silver salt of methyl- $\alpha$ -D-galacturonoside in poor yield to a syrup which was probably L-arabotrihydroxyglutaric dialdehyde.

### INTRODUCTION

In connection with a study of the action on pectic acid of agents used for delignifying wood and for bleaching cellulose, it seemed desirable to conduct some preliminary experiments with D-galacturonic acid and its methyl- $\alpha$ -glycoside methyl ester. The presence of the carboxyl group in the sixth position of these substances would be expected to make the fifth position more readily oxidizable than the corresponding position in non-acidic carbohydrates. As Link and his collaborators pointed out (1), oxidation of uronic acids with periodic acid yielded a dialdehyde in which the fifth position lay between an aldehyde and the carboxyl group. Such enhancement of the effect produced by the carboxyl group alone probably explained why the fifth position was then oxidizable even by an agent as mild as periodic acid. This assumption received solid support from later work on the overoxidation of uronides (2, 3), and the oxidation of the methylene group in malonic acid (4) by periodate; also from the oxidation of acetylacetone by lead tetraacetate (5). D-Galacturonic acid was, of course, oxidized by many agents to mucic acid, and could also be degraded in high yield to L-araboglutaric acid even by oxygen in aqueous barium hydroxide (6).

In the present experiments, a solution of pure galacturonic acid in a 10-fold molar amount of aqueous sodium chlorite buffered near pH 2.8 was kept at 70–75° for 150 minutes. These conditions resembled those used for delignifying wood meals by Wise's method (7). After excess oxidant and all cations were removed by appropriate methods described below, the solution was concentrated and the mucic acid that separated was removed. The concentrate was then resolved into its components by passage through a column of anion-exchange resin followed by paper partition chromatography. Galacturonic acid, DL-tartaric acid, and tartronic acid were recovered in pure crystalline form, the identities of the last two being confirmed by preparing the crystalline di-*p*-nitrobenzyl ester, and the crystalline dimethyl ester, respectively. The recovery of unchanged galacturonic acid was unexpected, because the conditions of the oxidation would have oxidized the aldehyde group in glucose (8) or in veratraldehyde (9) swiftly and almost quantitatively to carboxylic acid.

<sup>1</sup>Manuscript received July 13, 1959.

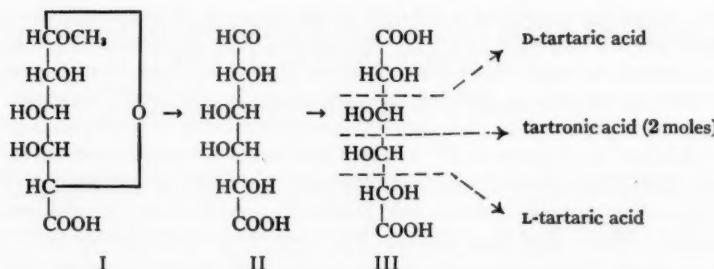
Contribution from the Division of Industrial and Cellulose Chemistry, McGill University, and the Wood Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Quebec. Abstracted from the Ph.D. thesis submitted by R.H.Z. to the University in April, 1959.

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A similar oxidation employed a 10-fold molar amount of aqueous chlorine dioxide, buffered near pH 2.7 and kept at 70–75° for 150 minutes. Some unchanged galacturonic acid was recovered, as might have been expected from the resistance of glucose to oxidation with chlorine dioxide at 20° (8); also some mucic acid and DL-tartaric acid, but tartronic acid was absent. The pure, crystalline methyl ester of methyl- $\alpha$ -D-galacturonoside, when oxidized for 2 hours at 25° with a 3-fold molar amount of sodium hypochlorite at pH 11.5, yielded DL-tartaric acid and tartronic acid, but, in addition, acidic methyl- $\alpha$ -D-galacturonoside and galacturonic acid itself, all of which were crystallized and carefully identified. Mucic acid was absent. The appearance of galacturonic acid in this experiment was attributed to oxidation, since small amounts of glucose were isolated from methyl- $\beta$ -D-glucopyranoside (10) and cellulose (11) oxidized with hypochlorite at pH 4–4.5. When the methyl ester methyl glycoside of galacturonic acid was kept at 25° for several hours in 1% sodium hydroxide (pH 12), free galacturonic acid formed only if traces of air were present. This observation contrasted sharply with the relatively great resistance of uronosides to acid hydrolysis (12) and with the claim that methyl- $\alpha$ -D-galacturonoside and its methyl ester were both non-reducing to Fehling's solution (13). Although the methyl ester of methylglucopyranuronoside was also non-reducing and required the proper amount of alkali when saponified, the 3,6 lactones of methyl- $\beta$ -D-glucofuranoside and 1,2-di-*O*-isopropylidene glucofururonic acid both reduced Fehling's solution and slowly neutralized more than the theoretical amount of alkali (14). The instability toward alkali of methyl pectate was discussed in the review by Whistler and BeMiller (15). In the present case, the action of alkali alone on galacturonic acid, its methyl glycoside, and methyl glycoside methyl ester, could well be the subject of a separate research. After treatment with 1% sodium hydroxide, the product from the methyl glycoside methyl ester, for example, yielded paper chromatograms showing only the spots characteristic of the acidic methyl glycoside and of galacturonic acid, and there was no clear evidence of either saccharinic acids or Lobry de Bruyn inversion products derived from galacturonic acid. Chromatographic evidence of such inversion products would be expected if an aldohexose had been submitted to the same conditions.

Since the only tartaric acid isolated in the above three oxidations was the DL-isomer, whose purity and optical inactivity were always carefully checked, it followed that the galacturonic acid or its methyl glycoside had been cleaved at equal rates at the 2,3- and 4,5-positions. Such symmetrical cleavage suggested that one of the initial products of oxidation was mucic acid, whose symmetry made it inevitable that the 2,3- and 5,6-positions would be equally liable to further oxidation. Oxidative cleavage at the 3,4-position would give the tartronic acid found. Mucic acid, when oxidized with chlorine dioxide, did, in fact, yield paper chromatograms with the spot characteristic of DL-tartaric acid; oxidation with chlorite and with alkaline hypochlorite yielded traces of tartronic acid, as well as of DL-tartaric acid. Structures I, II, and III illustrate these suggestions. Parallel test oxidations with glucurone showed that the phenomena discussed above were probably valid for uronic acids in general, though, of course, the products from glucurone were not the same as those from galacturonic acid.

When butanol – formic acid – water was the solvent in paper chromatography, the  $R_F$  values for galacturonic acid, its methyl- $\alpha$ -glycoside, DL-tartaric acid, and tartronic acids were well spaced at 0.04, 0.11, 0.21, and 0.38–44, respectively, and these compounds were easily distinguished from each other. A series of small-scale oxidations of galacturonic acid yielded chromatograms with spots at one or more of the four positions but no chromatogram contained additional spots at other  $R_F$  values. The chromatograms



were also sprayed with *o*-aminodiphenyl to detect any carbonyl compounds formed, but the results were uniformly negative. Although all of the oxidants tried thus yielded one or more of the same acids, and no others, it should be emphasized that the yields were small, and that any non-reducing, non-acidic products would not have been detected. As before, mucic acid was isolated directly from the concentrated liquors.

The results (Table I) showed that the behavior of chlorine dioxide depended to some extent on the hydrogen ion concentration of the solution. The production of some mucic acid near pH 1.3 agreed with the slow conversion of aldoses to aldonic acids by this

TABLE I  
Oxidation products from D-galacturonic acid and its methyl- $\alpha$ -glycoside methyl ester<sup>a</sup>

Aqueous oxidant	Unchanged acid	Mucic acid	Sugar acids <sup>b</sup>	
			<i>R<sub>F</sub></i> 0.21	<i>R<sub>F</sub></i> 0.38-0.44
Chlorine dioxide, 10 moles <sup>c</sup> at 75°				
Uronic acid, pH 1.3-1.4	+++	++	+	0
pH 2.6-2.9	+++	+	+	0
pH 4.5-4.8	+++	+++ <sup>d</sup>	++	0
pH 9 <sup>e</sup>	+++	0	+	0
Sodium chloride, 10 moles at 75°				
Uronic acid, pH 2.3-2.9	+++	+++	+	+++
Chlorine, large excess near 0°				
Uronic acid, pH ~ 5	+++	+	+	0
Hypochlorite, 3 moles <sup>c</sup> at 25° and pH 10-11				
Uronic acid	++	+++	++	+++
Methyl glycoside ester <sup>f</sup>	++	0	++	+++
Hydrogen peroxide, 1.1 moles <sup>c</sup> at 25° and pH 9-12				
Uronic acid	+++	0	0	0
Methyl glycoside ester <sup>f</sup>	++	0	+	0
Sodium hydroxide, excess at 25° and pH 12 (1%) <sup>f</sup>				
Methyl glycoside ester <sup>f</sup>	++	0	0	0

<sup>a</sup>Oxidations lasted 90 or 150 minutes. A relatively large or intense spot on paper chromatogram denoted by +++; a fair amount by ++; a trace by +.

<sup>b</sup>DL-Tartaric acid, *R<sub>F</sub>* 0.21; tartaric acid, *R<sub>F</sub>* 0.38-0.44 with butanol-formic acid-water system.

<sup>c</sup>Per mole of uronic acid or uronide.

<sup>d</sup>Mucic acid yield 20%, and maximum yield of tartaric acid.

<sup>e</sup>Spot for unchanged methyl glycoside methyl ester ++ at *R<sub>F</sub>* 0.11.

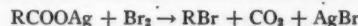
<sup>f</sup>For several hours; traces of air were probably present.

oxidant in strongly acidic conditions (8), but a maximum formation of mucic acid and DL-tartaric acid near pH 4.5 was not anticipated. The generalization (16) that chlorine

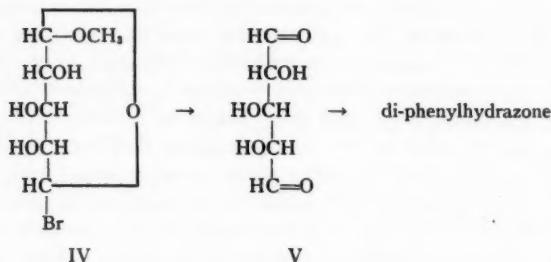
dioxide had no effect on sugars and polysaccharides thus did not apply strictly to galacturonic acid. Attempts to oxidize galacturonic acid at room temperature in a sodium borate buffer at pH 9, in 1% ammonium hydroxide (pH 10.5), or by continuously bubbling the gas through an ammonium hydroxide-sodium hydroxide solution kept near pH 12, yielded little or no mucic acid, and only traces of tartaric acid. As expected (8, 9), sodium chlorite readily oxidized the aldehyde group in galacturonic acid to give mucic acid as a major product, but the other major product was tartronic acid, no trace of which had been observed at any pH when the oxidant was chlorine dioxide. The result supported the opinion (8, 9) that sodium chlorite was an oxidant in its own right, and its effects could not be completely attributed to by-product chlorine dioxide. The possibility that the latter was exclusively responsible for the trace of DL-tartaric acid formed was not investigated.

Only traces of oxidation were observed when chlorine gas was bubbled through a solution of galacturonic acid kept near 0° and pH 5, conditions reminiscent of those used to delignify wood by one or other of the chlorination processes (17, 18). At pH 10-12 and 25°, however, hypochlorite produced relatively extensive oxidation to mucic and tartronic acids, with lesser amounts of DL-tartaric acid, and thus resembled acidified sodium chlorite in its action. The resemblance included the survival of some of the galacturonic acid in circumstances where glucose would have been rapidly and almost quantitatively oxidized to gluconic acid. Alkaline hydrogen peroxide appeared incapable of oxidizing galacturonic acid at 25°, although some of this acid was produced from the corresponding methyl- $\alpha$ -glycoside methyl ester. As in the case of alkaline hypochlorite, the loss of the glycosidic methyl group was tentatively attributed to the oxidant rather than to the alkalinity.

Kleinberg (19) reviewed the degradation of the anhydrous silver salts of many organic acids to the lower halides by elemental chlorine, bromine, or iodine,



and the reaction was extended to alginic acid, penta-*O*-acetyl gluconic acid, and an oxycellulose acetate by Rice and Johnson (20). A mixture of the anhydrous acid chloride and silver oxide could be substituted for the silver salts in these reactions (20). Since salts of simple uronic acids had apparently not been degraded in this way, a few preliminary experiments were carried out with galacturonic acid and its methyl glycoside. Little or no action occurred when dry calcium galacturonate was suspended in carbon tetrachloride containing an equimolar amount of bromine. The same reagent, however, caused the quick evolution of carbon dioxide from the silver salt of methyl- $\alpha$ -D-galacturonic acid. Extraction of the product with water gave a neutral, strongly reducing solution, free of silver and bromide ions, from which a clear syrup was isolated by paper chromatography. This syrup was free of methoxyl groups and yielded a crystalline phenylhydrazone melting at 128-129°. By analogy with the earlier work, the methyl galacturonide (I) would first be degraded to an acetobromo derivative (IV), which probably decomposed during isolation to yield the methoxyl-free dialdehyde (V). The yield of the crystalline di-phenylhydrazone, however, was only 8-10% of theory, the compound was not pure, and the work was discontinued. The product appeared to be of the same type as the xylotrihydroxyglutardialdehyde bis-phenylhydrazone derived from the oxidation of 1,2-*O*-isopropylidene-D-glucofuranose with lead tetraacetate (21) or sodium periodate (22, 23).



## EXPERIMENTAL

All solutions and eluents were concentrated in a rotatory film evaporator under diminished pressure at not more than 50°. Melting points were corrected and analyses were quoted as the mean of concordant determinations.

## Materials and Methods

The methyl ester of methyl- $\alpha$ -D-galacturonopyranoside monohydrate was prepared by boiling crystalline D-galacturonic acid, 25 g, in methanolic hydrogen chloride (13, 24), and after recrystallization from water had m.p. 142–144°, and specific rotation in water  $[\alpha]_D^{20} +122^\circ$  ( $c$ , 1.0%).

To prepare the silver salt, 1.1 g of the methyl ester was saponified by solution for 1 hour at room temperature in 50 ml of 0.1 *N* sodium hydroxide in a nitrogen atmosphere. Silver acetate, 0.72 g dissolved in 50 ml of hot water, was then added and a few minutes later the solution was filtered. Evaporation of the filtrate to small volume caused the white salt to separate. Yield, 0.7 g or 67%. Found: Ag, 33.5%. Calc.: Ag, 34.3%.

Di-(*p*-nitrobenzyl)-DL-tartrate, prepared from the crystalline disodium salt and *p*-nitrobenzyl bromide (25), after recrystallization from 63% ethanol melted correctly at 146–148°. The dimethyl ester of tartronic acid, also required for reference purposes, was prepared by boiling 0.1 g of the free acid under reflux for 2 hours in 3% methanolic hydrogen chloride. After removing halide ions as the silver salt and any residual cations by an ion-exchange resin, the liquid was concentrated and chilled. The crystalline dimethyl ester separated, and its melting point was correct at 43–45° (26).

Chlorine-free, 0.25-0.35 M solutions of chlorine dioxide were prepared from Schacherl's mixture of potassium chlorate, oxalic acid, and 33% sulphuric acid with the precautions noted elsewhere (27) and were standardized iodometrically. Chlorine dioxide was assumed to have five oxidizing equivalents in this standardization, whereas sodium chlorite had only four (27). Solutions of sodium hypochlorite were standardized either iodometrically or by the method employing arsenite.

Paper partition chromatography, employing Whatman No. 1 paper, and 10 lambda ( $10^{-2}$  ml) aliquots, was carried out by conventional methods. The solvent system was butanol - formic acid - water (500:115:385 vol.) (28), and the chromatograms after being dried *in vacuo* at 115° were sprayed with bromphenol blue in 90% ethanol (29). This spray gave yellow spots with sugar acids, and was stable indefinitely if stored in the dark at -10°. Residual traces of hydrochloric and chloric acids were retained at or near the starting line in these chromatograms. The best separations by column chromatography were obtained with a 50-100 mesh Dowex 1-4X anion-exchange resin which was converted from the chloride to the acetate form by washing in succession with 5% sodium hydroxide, water, *N* acetic acid, and water.

*Oxidations of D-Galacturonic Acid**(a) With Chlorine Dioxide*

Galacturonic acid, 18 g (93 mmole), was dissolved in a 10-fold molar amount of aqueous 0.3 M chlorine dioxide adjusted to pH 5 with acetic acid and kept at 70–75°. After 150 minutes the solution was cooled, and excess chlorine dioxide was removed by the passage of nitrogen gas. Concentration then caused the separation of crystalline mucic acid, decomp. 214–217°, and a paper chromatogram of the filtrate showed it to contain only unchanged galacturonic acid,  $R_F$  0.04, a tartaric acid,  $R_F$  0.21, and traces of inorganic acids.

A few grams of Dowex 1-4X anion-exchange resin (acetate form) was dispersed in the concentrate, and several hours later the resin with the absorbed acids was recovered and added to the top of a 102 cm  $\times$  5 cm column of the same resin. Elution of the column with water, and then with increasing concentrations of acetic acid, failed to remove any sugar acids until  $N$  acetic acid was used. Twelve 1-liter fractions then contained the galacturonic acid, which crystallized when the combined fractions were concentrated and chilled. After recrystallization, the galacturonic acid had the correct m.p., 158–159°, and the correct initial specific rotation of  $[\alpha]_D^{20} +97^\circ$  in 1% aqueous solution. The sample when oxidized with nitric acid gave mucic acid, decomp. 215–217°.

More concentrated acetic acid,  $N$  to 3  $N$ , failed to remove sugar acids from the column, but elution with 0.5  $N$  trifluoroacetic acid, 100 ml fractions being collected, removed both DL-tartaric acid and inorganic acids. These eluates were combined, concentrated to a very small volume, and spotted on sheets of Whatman No. 3MM chromatography paper, 50 mg being in each spot. The portions of paper containing the tartaric acid were extracted with water, and the product crystallized from the concentrate. After recrystallization, the m.p., 203–204°, the neutralization equivalent, 75, and the optical inactivity in water ( $c$ , 1%) were correct for DL-tartaric acid. A mixed melting point with an authentic sample was undepressed, and the m.p., 146–148°, of the crystalline di-(*p*-nitrobenzyl)-DL-tartrate was also satisfactory.

Several experiments with 0.35-g samples of galacturonic acid were carried out at room temperature and different pH values, and the results were assessed by paper chromatograms (Table I). A larger quantity of acetic acid was used to maintain pH 1.3. The buffer for pH 5 consisted of acetic acid and 3.2% aqueous sodium acetate, the sodium ions being afterwards removed by Amberlite IR-120 cation-exchange resin. In an experiment at pH 9, 0.35 g of galacturonic acid was dissolved in 70 ml of a potassium chloride–boric acid–sodium hydroxide buffer (30), but as soon as 20 ml of 0.27 M chlorine dioxide was added the pH decreased and more sodium hydroxide had to be added. Two further additions of the same amount of chlorine dioxide were made at intervals of 30 minutes, with additions of alkali to maintain pH 9, and after 2 hours the solution was shaken with silver carbonate. Insoluble silver salts were removed, and the filtrate was evaporated to dryness. The residue was taken up in 100 ml of acidified methanol and the solution was evaporated to dryness; several such cycles sufficed to remove all boric acid as the volatile methyl ester. An aqueous solution of the residue was then prepared for chromatography by passage through Amberlite IR-120 cation-exchange resin. An experiment that yielded only a trace of tartaric acid,  $R_F$  0.21, consisted of adding a solution of 0.35 g of galacturonic acid in 100 ml of 1% ammonium hydroxide to 50 ml of 0.21 M chlorine dioxide (6-fold amount). After 2 hours at 70–75° the solution was colorless, but on acidification to pH 2–3 with acetic acid the characteristic odor and color of chlorine dioxide reappeared. A similar ammonia solution was kept at pH 12 by

the continuous addition of sodium hydroxide while chlorine dioxide was bubbled through it, but little or no oxidation of the galacturonic acid occurred.

(b) *With Sodium Chlorite*

A solution of galacturonic acid, 5.5 g, and 18.7 g of sodium chlorite (10-fold molar amount) in 1430 ml of 10% acetic acid (pH 2.7-2.9) was kept at 70-75° for 150 minutes. By-product chlorine dioxide then was expelled by the passage of nitrogen gas, and any remaining oxidizing agents were destroyed by the addition of a little cold, 48% hydriodic acid, the liberated iodine being promptly extracted with ether. After the removal of halides as the silver salts, the filtered solution was passed through a column of Amberlite IR-120 cation-exchange resin, and was concentrated. Mucic acid, decomp. 215-218°, separated, and after further concentration the filtrate was separated on a 91.5 cm × 5 cm column of Dowex 1-4X resin (acetate form) as described in the oxidation with chlorine dioxide. Galacturonic acid again crystallized from the *N* acetic acid eluates and after recrystallization had the correct melting point and specific rotation. Oxidation with nitric acid yielded mucic acid.

DL-Tartaric acid and tartronic acid occurred together in the 0.5 *N* trifluoroacetic acid eluates, and were separated by paper chromatography. After recrystallization, the DL-tartaric acid was optically inactive, melted correctly at 204-205°, had the correct neutralization equivalent, and yielded the crystalline di-(*p*-nitrobenzyl) derivative with the proper melting point. The tartronic acid solution was evaporated to dryness because no crystallization occurred on cooling of the concentrated liquor. A solution of the residue in water was evaporated to dryness several times to eliminate formic acid, and the tartronic acid then crystallized. After recrystallization from water, the product had the correct m.p., 141-143°, and neutralization equivalent, 61.0, and was optically inactive (water, *c*, 1%). Its identity was confirmed by conversion to dimethyl tartronate, m.p. 44-45°.

(c) *With Chlorine*

A solution of 0.35 g of galacturonic acid in 100 ml of water buffered to pH 5 with acetic acid - sodium acetate was kept near 0° while chlorine gas was bubbled through it for 10 minutes. Most of the gas was removed by the passage of nitrogen, and any residual oxidant was destroyed by the addition of a small amount of hydriodic acid, liberated iodine being extracted with ether. After neutralization with silver carbonate, the clarified liquor was passed through Amberlite IR-120 resin, and the cation-free effluent was concentrated. A small amount of mucic acid, decomp. 215-216°, separated, and after its removal the concentrate was chromatographed on paper.

(d) *With Sodium Hypochlorite*

Galacturonic acid, 0.35 g, was dissolved in 50 ml of water and the solution was adjusted to pH 11.7 with aqueous sodium hydroxide. After 8 ml of 0.75 *M* sodium hypochlorite (3-fold molar amount) had been added the mixture was kept at 25° for 2 hours, during which period the pH decreased to 11.3. The solution was acidified, treated with dilute hydriodic acid and silver carbonate, and freed of cations as described above. A large amount of mucic acid, decomp. 214-216°, was removed prior to chromatography.

(e) *With Hydrogen Peroxide*

A solution of 0.35 g of galacturonic acid in 100 ml of water, adjusted to pH 9.9 with aqueous sodium hydroxide, was mixed with 2 ml of 0.98 *M* hydrogen peroxide (1.1 molar amount), and kept at 25° for 90 minutes. After acidification with acetic acid, the excess oxidant was reduced by the addition of a little 48% hydriodic acid, 30 minutes

being required for this reaction to become complete. The iodine formed was extracted with ether. Neutralization, the removal of cations, and concentration yielded a solution containing unchanged galacturonic acid.

*Methyl- $\alpha$ -D-galacturonoside Methyl Ester and Sodium Hypochlorite*

Five grams of the crystalline methyl glycoside methyl ester monohydrate was oxidized at pH 11.7 and 25° with a 3-fold molar amount of aqueous sodium hypochlorite, and the products were recovered, as in the parallel oxidation of galacturonic acid. These products were: acidic methyl galacturonoside, m.p. 112–114°,  $[\alpha]_D^{20} +130^\circ$  in water (*c*, 1.0%); galacturonic acid, m.p. 158–159°, initial  $[\alpha]_D^{20} +97^\circ$  in water (*c*, 1.0%); optically inactive DL-tartaric acid (1% aqueous solution), neutralization equivalent, 75.8, and m.p. 203–204°; and optically inactive tartronic acid, m.p. 142–144°, and neutralization equivalent 61.0. All these constants were in good agreement with those of authentic samples.

*Attempted Decarboxylations with Bromine*

In a typical experiment, 1 g of the dry silver salt of methyl- $\alpha$ -D-galacturonoside, dispersed in 100 ml of anhydrous carbon tetrachloride, was treated with 0.3 ml, or the equimolar amount, of bromine (31). A rapid reaction occurred initially, with the evolution of some heat and carbon dioxide. After the mixture had been warmed for 10 minutes at the end of this reaction, the insoluble portion was washed with carbon tetrachloride and dried over silica gel. The yellow-white solid, 0.9 g, was extracted with three 75-ml volumes of water to remove insoluble silver salts. The combined extracts were free of silver and bromine ions, and gave a negative test for carboxylic acid groups, but a strongly positive test for aldehydic groups. No solid separated when the extracts were concentrated, but a small aliquot when chromatographed on paper yielded a single spot of  $R_f$  0.84 (butanol – formic acid – water system, *o*-aminodiphenyl spray).

An orange precipitate immediately formed when the above concentrate was mixed with 5 ml of water containing 0.5 g of phenylhydrazine hydrochloride and 0.8 g of sodium acetate. After being dried, this precipitate weighed 0.1 g (10%), and melted at 129–130°. Found: OCH<sub>3</sub>, 0.0; N, 23.7%. Calc. for the bis-phenylhydrazone of a trihydroxyglutardialdehyde, C<sub>17</sub>H<sub>20</sub>N<sub>4</sub>O<sub>3</sub>: OCH<sub>3</sub>, 0.0; N, 17.1%.

When the molar ratio of bromine to the silver salt of the methyl galacturonoside was doubled, the yield of the crystalline phenylhydrazone was 8%. Found: OCH<sub>3</sub>, 0.0; N, 20.5%.

ACKNOWLEDGMENTS

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# THE EXCHANGE OF OXYGEN-18 BETWEEN CELLULOSE, ADSORBED WATER, AND WATER VAPOR<sup>1</sup>

A. R. G. LANG AND S. G. MASON

## ABSTRACT

The adsorption on regenerated cellulose of water at vapor pressures of 0 to 40  $\mu$  Hg has been measured by an oxygen-18 dilution technique. The results showed that cellulose may be dried to less than 0.04% moisture by evacuation at 70° C. The adsorption isotherm was compared with that of Taylor for viscose rayon.

It was also shown that oxygen-18 does not exchange between cellulose and water.

## INTRODUCTION

The experiments described in this note provided supplementary information for a study of the exchange of tritium between cellulose and water vapor described elsewhere (1). In order to correct the experimental data for the exchange occurring between the water vapor and the water adsorbed on the cellulose even after prolonged evacuation, it was necessary to know the amount of water adsorbed under the conditions of the experiments.

The published values for the amount of adsorbed water present on cellulose at very low vapor pressures (2-5) actually represent the incremental adsorption above a certain minimum defined by the method of drying; there still exists, however, some doubt as to whether cellulose can be completely freed from adsorbed water. In the usual method of drying by heating to 105-110° C, in an air oven, up to 0.5% by weight of water remains as a result of the small but nevertheless significant water vapor pressure (6, 7). On the other hand, it is generally considered that cellulose is completely dried by prolonged desiccation over phosphorus pentoxide at room temperature (6) or at elevated temperatures (8), by heating in a stream of dry gas (8), or by extended evacuation (2-5, 7). However, in all these measurements the sole criterion of dryness was that the mass of cellulose had reached a minimum value. Recently it was reported from the direct titration of cellulose by the Karl Fischer reagent that 1% adsorbed water remained on cellulose dried over phosphorus pentoxide (9).

In the present experiments, these uncertainties were eliminated by measuring the dilution of oxygen-18 when oxygen-18-enriched water was mixed with the adsorbed water *in situ*. The method requires, however, that the oxygen atoms of cellulose do not exchange with those of water, and it was therefore first necessary to determine whether or not such exchange was taking place.

Oxygen-18 generally does not exchange between alcohols and water (10). However, only one author (11) has studied the system cellulose/water and a critical study of his data showed that less than 6% of the cellulose oxygens reacted. Since this precision was inadequate for the present work, it was necessary to extend the measurements.

## PROCEDURE

In the method used, known quantities of dried cellulose and O<sup>18</sup>-enriched water were reacted together, the water recovered, and the dilution of the O<sup>18</sup> measured mass spectrometrically. Dilution could be caused both by exchange with the oxygen atoms of the

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Contribution from the Physical Chemistry Division, Pulp and Paper Research Institute of Canada, Montreal, Que., and the Department of Chemistry, McGill University, Montreal, Quebec.

cellulose molecules, and by mixture with adsorbed water. The quantities were chosen so that an adsorption of 1 mg water per g cellulose would cause a 10% change in the concentration of  $O^{18}$ .

Figure 1 shows the apparatus. It was made of brass and copper, except for the Pyrex glass jacket (F) of the trap and the tared recovery tube (H). The train could be broken at E so that the reaction vessel could be connected directly to the vacuum system, which

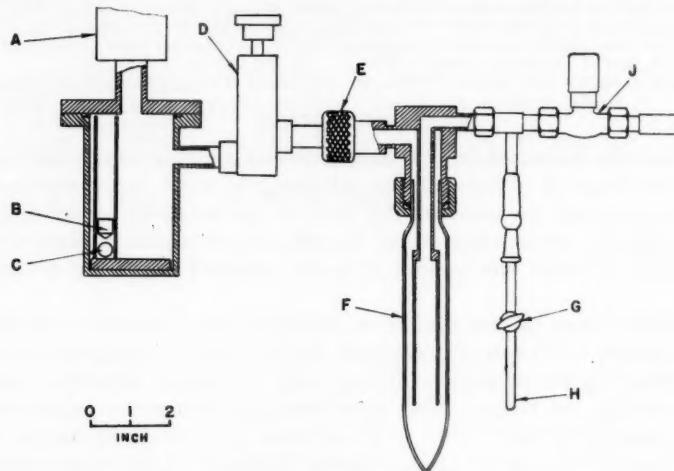


FIG. 1. Apparatus. A, Pirani gauge; B, plunger; C, ampoule; D, valve; E, vacuum coupling; F, trap; G, stopcock; H, tared glass tube; J, valve.

consisted of a mechanical pump, a two-stage oil diffusion pump, and a liquid-air trap.

Air-dried gel cellulose film was used, made from viscose and neither plasticized nor coated. This sample was identical with sample *c* used previously (1). For each experiment, strips 7.5 cm wide by  $23\ \mu$  thick and weighing 2 g on a dry basis (oven-dried at  $105^\circ\text{C}$ ) were folded backwards and forwards on themselves and placed in the reaction vessel together with a thin-walled Pyrex ampoule (C) containing 0.02 g of water having an O atom content of 9.4%  $O^{18}$ . The masses of cellulose and water (with the necessary correction for buoyancy of the evacuated ampoule) were determined within 1%.

The cellulose was dried to various degrees by evacuating the reaction vessel. In one case the reaction vessel was heated to about  $70^\circ\text{C}$  during the reaction; in all other cases the temperature was about  $25^\circ\text{C}$ . Details including times of evacuation are given in Table I. After the evacuation, the cellulose was isolated by closing valve D, and the gas pressure was measured at intervals for a total time of up to 3 hours with an Edwards Pirani gauge, Type MA-5 (A, in Fig. 1), which had been calibrated against a McLeod gauge. Since the empty reaction vessel leaked air ( $0.071\ \mu\text{Hg}$  per minute), the equilibrium water vapor pressure was obtained as follows: The pressure was plotted against time to yield curves illustrated in Fig. 2. When the slope of a curve reached the constant value of  $0.071\ \mu\text{Hg}$  per minute, measurements were discontinued; the linear part of the graph was then extrapolated back to zero time and the intercept on the pressure axis taken as the equilibrium water vapor pressure.

To bring about the exchange the reaction vessel was shaken until the stainless steel plunger (B, Fig. 1) broke the ampoule of water (C). The reaction continued for 8 to 8.5

TABLE I  
Adsorption of water on cellulose at low vapor pressures

Experiment	Sample	Evacuation Time, hours	Temp., °C	P equilibrium H <sub>2</sub> O, μ Hg	Oxygen-18 in recovered water, atom fraction	m/M*	Water adsorbed at P, mg/g
1	Blank	21	25	0	0.0941	—	0
2	Cellulose	59	70	< 0.1	0.0932	0.0089	0.10
3	Cellulose	47	23	4	0.0815	0.0104	1.61
4	Cellulose	40	24	6.5	0.0693	0.0099	3.52
5	Cellulose	35	25	16	0.0681	0.0104	3.95
6	Cellulose	23	27	41	0.0589	0.0108	6.46

\* $m/M$  = (mass of water in ampoule, g)/(mass of dry cellulose, g).

hours at 23 to 27° C, and then the water was collected by evacuating the reaction vessel through the trap (F) cooled with a Dewar flask of liquid air. Valves D and J were then closed and the Dewar of liquid air moved from the trap to the lower end of the tared tube (H) so that the water distilled into it. Stopcock G was then closed and the tared tube (H) removed from its matching ground-glass joint and weighed. Between 50 and 60% of the total water reacted with the cellulose was recovered. The isotope effect in this distillation is negligible: calculations assuming the extreme case of equilibrium distillation (1) and using the values of the vapor pressures of the H<sub>2</sub>O<sup>18</sup> and H<sub>2</sub>O<sup>16</sup> given by Huffman and Urey (12) show that the concentration of O<sup>18</sup> in the distillate after 50% recovery is the same (within 0.6%) as before distillation.

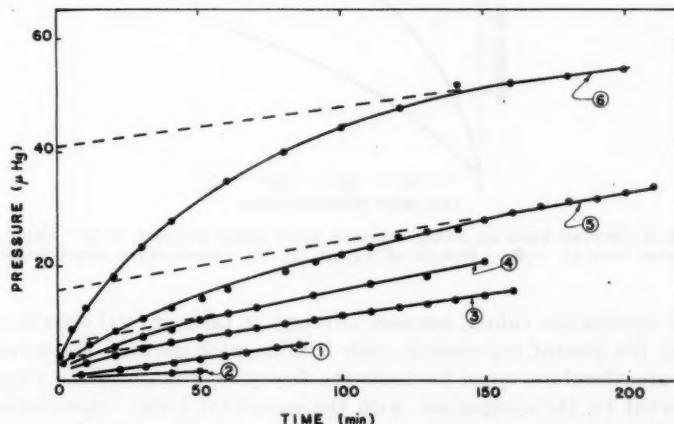


FIG. 2. Estimation of equilibrium pressure. Circled figures are experiment numbers.

The concentration of the O<sup>18</sup> in the water in tube H was determined by the method of Dostrovsky and Klein (13). The water was exchanged with carbon dioxide, then the ratio of the 44/46 mass peaks of the carbon dioxide was measured four times in a mass spectrometer. The concentration of the O<sup>18</sup> in the water was calculated from relationships given by Dostrovsky and Klein.

#### RESULTS AND DISCUSSION

The results are summarized in Table I.

When the sample was evacuated until the vapor pressure was practically zero (experi-

ment 2), almost no dilution of the  $O^{18}$  occurred. This experiment showed simultaneously that no exchange occurred between the oxygen atoms of the water and the cellulose (less than 0.08% of the cellulose oxygens), and that no water (less than 0.4 mg per g) remained adsorbed in the cellulose. The amount of adsorbed water on the cellulose for experiments 2 to 6 was therefore given from an  $O^{18}$  balance as:

$$A = \frac{m}{M} \{ (N_i/N_f) - 1 \}$$

where  $A$  is the adsorbed water (milligrams per gram of cellulose),  $m$  the mass of water in the ampoule (milligrams),  $M$  the mass of cellulose on an oven-dry ( $105^\circ C$ ) basis (grams), and  $N_i$  and  $N_f$  the initial and final atom fractions of  $O^{18}$ .

The zero adsorption of water in experiment 2 removed any reasonable doubt that cellulose can be completely dried by evacuation with heat. Since this fact was assumed in the low-pressure adsorption studies of Taylor (2, 3, 4) and Neale and Springfellow (5) its establishment adds reliance to their experimental values.

Figure 3 shows the relationship between the amount of adsorbed water and the estimated vapor pressure. Except for the zero value the vapor pressures were probably less

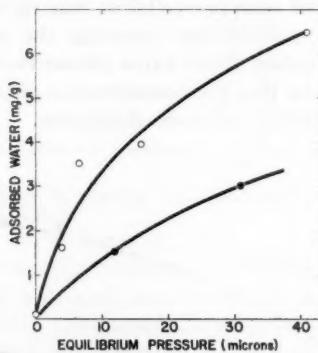


FIG. 3. Graph of adsorbed water on cellulose versus water vapor pressure. —○— Oxygen-18 dilution method (desorption branch). —●— Results of Taylor (2) for viscose rayon (reproducible adsorption branch).

than the true equilibrium values, because, although it takes several days to reach equilibrium (2), in the present experiments only 3 hours were allowed. The sorption values reported here are, therefore, upper limits for the desorption branch of the sorption cycle. This is supported by the comparison with the somewhat lower "reproducible adsorption" values for viscose rayon reported by Taylor (2), who also demonstrated that appreciable sorption hysteresis occurred at these low pressures.

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## THE MERCURY-PHOTOSENSITIZED DECOMPOSITIONS OF PROPANE AND ETHANE<sup>1</sup>

R. A. BACK<sup>2</sup>

### ABSTRACT

The mercury-photosensitized decompositions of propane and ethane have been studied at pressures of 300 and 600 mm, at 24° C, at very low conversions. Hydrogen was the only product identified and measured. The hydrogen yield fell rapidly at first, with increasing time of irradiation, and finally became constant. This behavior is attributed to the accumulation in the system of propylene or ethylene formed by the disproportionation of propyl or ethyl radicals, and the constant rate of hydrogen production finally achieved is thought to correspond to a steady-state concentration of the unsaturate. Previous values of the quantum yields of these decompositions were probably measured in this steady-state region, and must be corrected upwards.

Relative values have been estimated for the various rate constants involved in this mechanism. There is some evidence that energy-rich radicals, formed by the addition of hydrogen atoms to the unsaturates, tend to disproportionate rather than dimerize.

### INTRODUCTION

In a previous study of the mercury-photosensitized decomposition of *n*-pentane at very low conversion, the hydrogen production decreased rapidly at first, then more slowly, and finally became constant after about 0.5% reaction (1). This was attributed to the accumulation in the system of pentene, formed by disproportionation of pentyl radicals, and the final constant rate of hydrogen production was thought to correspond to a low, steady-state concentration of pentene. The hydrogen yield was reduced, and pentene consumed, by the addition of hydrogen atoms to pentene. Similar behavior has been observed with the cyclo-alkanes (2), and more recently with *n*-butane (3). Previous studies of the mercury-photosensitized decomposition of propane and ethane did not show this effect, as hydrogen production was independent of time (4). However, rough calculations from the relative rates of the reactions concerned suggest that even the smallest conversions achieved in these experiments were probably much too large for the initial behavior to be observed. It was decided to study these reactions at very low conversions to see whether they behaved in the same way.

### EXPERIMENTAL

The apparatus, a conventional static system, and the method were essentially similar to those described previously (1). Two reaction vessels, of 38- and 180-cc volume, were used in the course of the work, the larger volume permitting measurements to be made at lower conversion. After irradiation, gases non-condensable at -210° C were removed and analyzed, and the hydrocarbon, together with any condensable products, was returned to the reaction vessel for further irradiation. In this way, the hydrogen yield could be studied as a function of total irradiation time, using a single sample of hydrocarbon. Concentrations of hydrogen and unsaturates produced in the system were always low enough so that all quenching of the excited mercury atoms was by the hydrocarbon alone. Measurements were made with propane at 300- and 600-mm pressure, and with ethane at 305-mm pressure, all at 24° C. In some experiments, unsaturates (propylene or ethylene) were added.

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Phillips Research-grade propane was used without further purification. A sample treated with  $\text{HgSO}_4\text{-H}_2\text{SO}_4$  solution to remove unsaturates gave the same results as the untreated gas. Phillips Research-grade ethane was found to contain appreciable amounts of methane and ethylene. The former was removed by repeated trap-to-trap distillation and prolonged pumping at  $-210^\circ\text{C}$ . The latter was removed by condensing the ethane onto charcoal previously treated with bromine.

## RESULTS

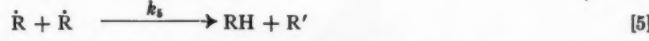
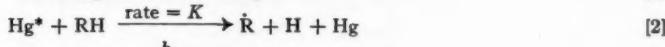
### Propane

The non-condensable gas was never less than 99.5% hydrogen, measured by diffusion through a Pd thimble at  $300^\circ\text{C}$ . Careful analysis with a low temperature still failed to detect any  $\text{C}_2$  hydrocarbons, so that hydrogen was the only product detected and measured. Hydrogen yield is shown as a function of total time of irradiation in Figs. 1 and 2 for propane at 600- and 300-mm pressure respectively. The effect of adding propylene to the system is shown in Fig. 3.

### Ethane

When care was taken to remove all the methane present initially, the non-condensable gas produced was never less than 99% hydrogen, and this was again the only product detected and measured. The hydrogen yield is shown in Fig. 4 as a function of total time of irradiation for ethane carefully purified to remove ethylene. For comparison, the hydrogen yield from Research-grade ethane, used without purification, is shown in the same figure.

Under conditions of high pressure, low light intensity, and low temperature, and consequent absence of hydrogen atom "cracking" reactions and other complicating processes, the simple mechanism suggested previously (1) seems to account adequately for the observed behavior of both compounds.



$\text{RH}$  is an alkane,  $\dot{\text{R}}$  is an alkyl radical, and  $\text{R}'$  is an olefin. As the olefin accumulates in or is added to the system, the following additional reactions may become important.



where  $\dot{\text{R}}'$  is an unsaturated radical,  $\dot{\text{R}}_2$  is a dimer radical, and  $\text{R}'_2$  is an unsaturated dimer. From the mechanism, it may be shown that

$$[1] \quad d\text{H}_2/dt = K(k_3[\text{RH}] + k_7[\text{R}'])/(k_3[\text{RH}] + (k_6 + k_7)[\text{R}']).$$

Thus  $d\text{H}_2/dt$  is equal to  $K$  initially, decreases as  $\text{R}'$  accumulates, and becomes constant if  $\text{R}'$  attains a steady-state concentration before depletion of  $\text{RH}$  becomes appreciable.

This behavior was shown by propane and ethane, Figs. 1, 2, and 4, and the reduction of the hydrogen yield in the steady state may be taken as a measure of the extent of reaction 6. Furthermore, if loss of  $R'$  via reaction 8 is neglected, the reduction of the hydrogen yield is also a measure of the rate of disappearance of  $R'$ , and since it is a steady state, of the rate of formation of  $R'$  by reaction 5. Thus we may obtain the relative rates of reactions 4 and 5 directly from Figs. 1, 2, and 4, as shown.

Interesting confirmation that the plateaux do represent steady-state concentrations of

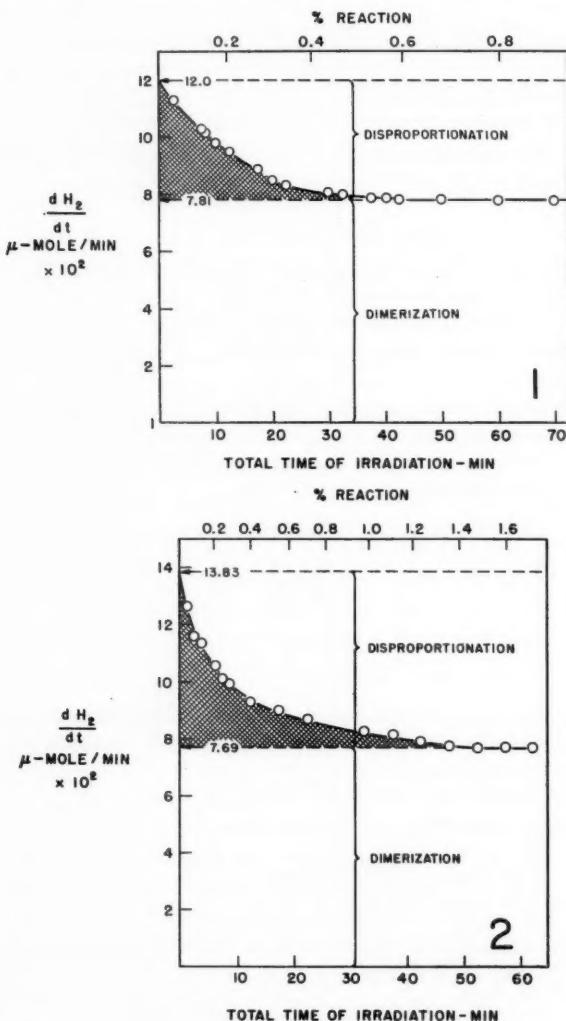


FIG. 1. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of propane at 600-mm pressure.

FIG. 2. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of propane at 300-mm pressure.

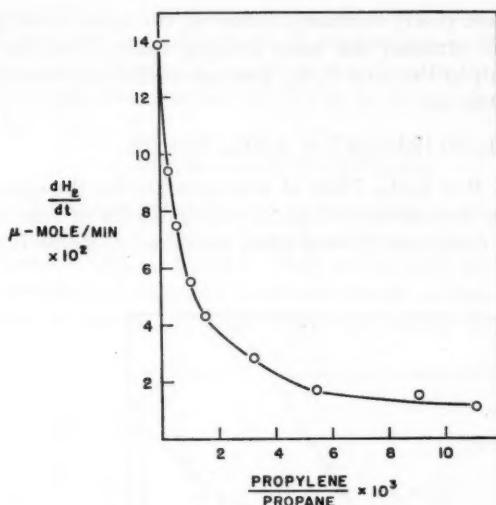


FIG. 3. The effect of added propylene on the rate of hydrogen production from the mercury-photosensitized decomposition of propane at 300-mm pressure.

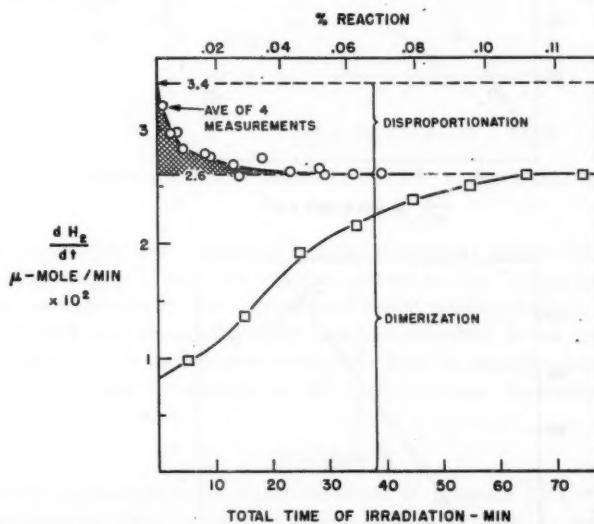


FIG. 4. Rate of production of hydrogen vs. total time of irradiation for the mercury-photosensitized decomposition of ethane at 305-mm pressure;  $\circ$  pure ethane,  $\square$  Research-grade ethane.

unsaturates is seen in the behavior of the impure Research-grade ethane (Fig. 4). Upon repeated irradiation, the ethylene in excess of the steady-state value was slowly used up, until finally the hydrogen yield rose to the same steady-state value as before. In another experiment, a sample of pure ethane was irradiated until the hydrogen yield had attained the plateau value. At this point, a small amount (0.02%) of ethylene was added, whereupon the hydrogen yield was reduced to 0.0042 micromoles/minute. Upon repeated

irradiation, the hydrogen yield slowly increased, following the same curve as the sample of impure ethane, and again attained the same limiting value. Thus the same steady state, which is a function only of the ratio  $k_4/k_5$ , was approached in three different ways.

Equation 1 may be rewritten as

$$[2] \quad (K - \frac{dH_2}{dt}) [RH]/[R'] = A(dH_2/dt) - BK$$

where  $A = (k_6 + k_7)/k_3$  and  $B = k_7/k_3$ . Plots of this equation for the experiments with propane-propylene mixtures are shown in Figs. 5 and 6. Ratios of rate constants calculated from the slopes and intercepts of these plots are shown in Table I, together with values of  $k_6/k_4$ .

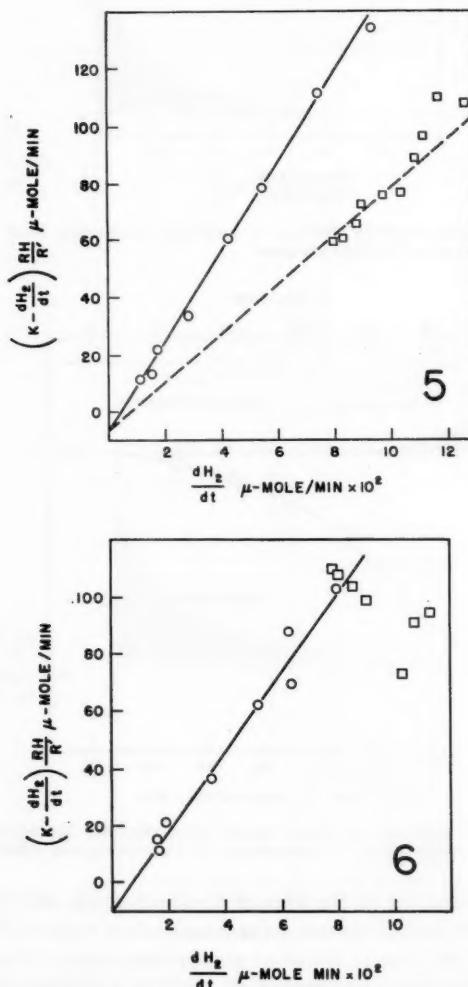


FIG. 5. A plot of equation 2 for propane at 300-mm pressure;  $\square$  pure propane,  $\circ$  added propylene.  
 FIG. 6. A plot of equation 2 for propane at 600-mm pressure;  $\square$  pure propane,  $\circ$  added propylene.

The same ratios of rate constants may be calculated in a different way from the experiments with pure propane and ethane. If one assumes a constant rate of formation of  $R'$  by reaction 5, and a loss of  $R'$  equal at any time to the net decrease in hydrogen production (thus neglecting reaction 8), it may be shown that the net rate of production of  $R'$  is given by

$$[3] \quad dR'/dt = d_2H/dt - (dH_2/dt)_S$$

where  $(dH_2/dt)_S$  is the rate of production of hydrogen in the steady state.  $R'$  may then be evaluated as a function of time by a graphical integration of this equation, represented by the shaded areas in Figs. 1, 2, and 4. Using values of  $R'$  obtained in this way, the data were plotted according to equation 2 and are shown in Figs. 5 and 6, for propane, and Fig. 7 for ethane. A similar graphical integration of the data for the impure ethane,

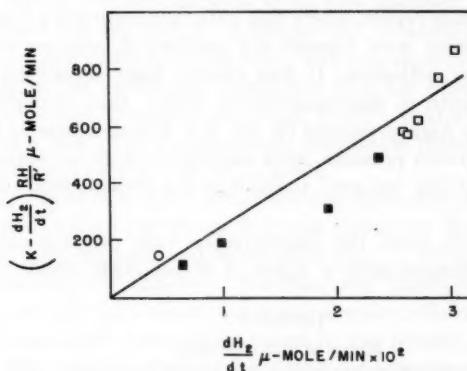


FIG. 7. A plot of equation 2 for ethane at 305-mm pressure; □ pure ethane, ■ Research-grade ethane, O added ethylene.

integrating backwards from the steady state, permitted calculation of ethylene concentrations in this system. These data are also plotted in Fig. 7, together with a single point obtained in the experiment, mentioned previously, when ethylene was added to ethane already irradiated until the steady state had been reached. From the pure ethane data, a rough value of  $k_6/k_3 = 25,000$  was estimated from a straight line drawn through the origin (since  $k_7$  is zero for ethylene). All ratios of rate constants are summarized in Table I.

#### DISCUSSION

The mercury-photosensitized decompositions of propane and ethane both show the same initial behavior that has been observed with *n*-pentane (1), *n*-butane (3), and some cyclo-alkanes (2). Because of the larger values of  $k_6/k_3$ , this was observed only at very low conversions (shown as upper abscissae in Figs. 1, 2, and 4). This was especially true for ethane, with which the steady state was attained after about 0.05% reaction, with an estimated steady-state concentration of ethylene of one part in 80,000. All previous studies of these reactions, in which hydrogen production was observed to be linear with time, were undoubtedly made in the steady-state region, and the measured quantum yields must be corrected upwards by the factor  $(k_4+k_5)/k_4$ , as indeed the authors anticipated. Bywater and Steacie reported a pressure-independent quantum yield of 0.50

for hydrogen production from propane at high pressures and room temperature (4), from which values of the initial quantum yield of 0.90 and 0.77 at 300 and 600 mm, respectively, may now be estimated. It may be noted that while the steady-state hydrogen yields at the two pressures are almost identical, confirming the pressure independence observed by Bywater and Steacie, the initial quantum yield appears to decrease with increasing pressure, suggesting, perhaps, the intermediate formation of an excited propane molecule of appreciable lifetime in the primary process. The quantum yields for the ethane decomposition reported by Darwent and Steacie (4), which tended towards unity at high pressure, should be revised upward in a similar way, although the correction here is smaller than for propane.

Values of  $k_5/k_4$  for both ethyl and propyl radicals appear to be rather higher than those observed for thermally equilibrated radicals (5, 6, 7, 8). Some of this discrepancy may be attributed to inaccuracy in the extrapolation to zero time. However, it should be noted that in the steady-state region, where this ratio is estimated, a fraction  $k_5/2(k_5+k_4)$  of the radicals in the system were formed via reaction 6, and would be vibrationally excited until stabilized by collisions. It has clearly been shown by several authors that such "hot" radicals tend to disproportionate rather than dimerize, and that these effects can persist to quite high pressures (9, 10, 11). The decrease in  $k_5/k_4$  for propane in going from 300- to 600-mm pressure lends support to such an explanation. It might be noted, incidentally, that the "propyl" radicals in the present study are very probably isopropyl radicals (9).

Values of  $k_6/k_3$  obtained from the experiments with propane-propylene mixtures (Table I) are in fair agreement with a value of about 3000 which may be estimated

TABLE I  
Ratios of rate constants

Hydrocarbon	$k_6/k_3$	$k_7/(k_6+k_7)$	$k_5/k_4$
Propane, 300 mm	1515	0.032	0.08
Propane, 600 mm	1304	0.061	0.54
Ethane, 305 mm	25000	—	0.31

from separate measurements of the two rate constants by Schiff and Steacie (12), and Bradley, Melville, and Robb (13). The values of  $k_7/(k_6+k_7)$ , the fraction of hydrogen atoms reacting with propylene which abstract hydrogen (Table I), are rather lower than previous estimates of this ratio (14). The variation with pressure is probably not significant, considering the relatively long extrapolation which is involved.

The data from the experiments with pure propane at 300 mm, plotted in Fig. 5, using calculated values of the propylene concentration, lie considerably below the data from the experiments with added propylene, and, taking the same intercept, would lead to values of  $k_6/k_3$  about half as large. A similar behavior was previously observed with *n*-pentane at 300 mm, which was tentatively attributed to the formation of 2-pentene in the disproportionation reaction (1). Such an explanation is impossible with propylene, and another cause must be sought. The values of the propylene concentration were calculated assuming, first, disappearance of propylene by reaction 6 only, and secondly, a constant rate of formation of propylene equal to that in the steady state. If propylene disappeared by other reactions, such as 8, or by direct photosensitized decomposition, the calculated values of propylene concentration would be too high, and  $k_6/k_3$  would be low, as observed. It is doubtful, however, that reaction 8 would occur to such an extent,

and the very low concentrations of propylene eliminate the possibility of direct decomposition. It may be noted that the reaction sequence, 7+9, would merely substitute hexene for propylene, which would not have a large effect.

The second assumption, that the rate of production of propylene is constant, is more likely at fault. The high value of  $k_5/k_4$  noted previously was attributed to preferential disproportionation of "hot" propyl radicals formed by reaction 6. Initially, however, all the propyl radicals were formed by reactions 2 and 3, and reaction 6 only becomes important as propylene accumulates in the system. Thus if "hot" propyl radicals were the cause of the high values of  $k_5/k_4$  in the steady state, the rate of formation of propylene may have been much lower in the earlier stages of the reaction, and the graphical integration may have thus overestimated the concentration of propylene quite considerably. In support of this explanation is the improved agreement of the two sets of data at 600-mm pressure, where a lower value of  $k_5/k_4$  was observed, and, presumably, "hot" radical reactions were less important. It seems that a similar explanation is probably valid for *n*-pentane. With ethane, at 305 mm, only one experiment was done with added ethylene, and it again lies somewhat above the data for pure ethane using calculated concentrations of ethylene. It should be noted, finally, that all these data for low concentrations of unsaturates lie in an inherently inaccurate region for the plot of equation 2, towards the right-hand side of Figs. 5, 6, and 7.

The value of  $k_6/k_3$  of 25,000, calculated from the data obtained with pure ethane, may also be compared with values calculated from the literature. Berlie and LeRoy measured  $k_3$  over a range of temperature, and from their data a collision yield of  $4.5 \times 10^{-8}$  at 24°C may be estimated (15). Bradley, Melville, and Robb estimated a collision yield of  $9.3 \times 10^{-5}$  for reaction 6 (13), which, assuming similar collision numbers, gives  $k_6/k_3 = 2100$ , an order of magnitude lower than found in the present study. Pursuing the discrepancy further, the collision yield of  $4.5 \times 10^{-8}$  for reaction 3, with ethane, is almost identical with the value  $4.6 \times 10^{-8}$  found by Schiff and Steacie for the same reaction with propane (12). From the results of Darwent and Roberts, however, a ratio  $k_3(\text{propane})/k_3(\text{ethane})$  of about 19, at 24°C, may be calculated (14). Taking a value of the ratio  $k_6(\text{propylene})/k_6(\text{ethylene})$  of 1.5 (13), from the present results a value of  $k_3(\text{propane})/k_3(\text{ethane})$  of about 25 may be estimated, in fair agreement with Darwent and Roberts, but much higher than the value of about 1 indicated from the combined results of Berlie and LeRoy, and Schiff and Steacie. One would expect the reaction of hydrogen atoms with the primary hydrogen atoms of ethane to be considerably slower than with the secondary hydrogen atoms of propane, and it would appear that the values of  $k_3$  (ethane) found by Berlie and LeRoy may be too high, as has been suggested elsewhere (16), although perhaps the discrepancies are simply an indication of the rather unsatisfactory knowledge of accurate absolute values for the rates of hydrogen atom reactions.

It may be noted that all the relative rate constants measured in the present work are dependent upon the values chosen for  $K$ , the initial rate of hydrogen production. The sharply rising nature of the curves (Figs. 1, 2, and 4) makes this extrapolation to zero time inherently inaccurate, while the presence of even minute amounts of unsaturates initially present in the hydrocarbon could seriously reduce the observed value of  $K$ . The reasonable agreement between values of  $k_6/k_4$  observed, and those measured by other methods suggests that the initial extrapolations were not grossly in error. The value of 0.9 for the initial quantum yield estimated for propane at 300 mm puts an upper limit on the possible value of  $K$  for that particular system. The reaction



[10]

may be of some importance, especially with ethane (6), and probably accounts for the decrease in quantum yield with decreasing ethane pressure observed by Bywater and Steacie (4). The occurrence of this reaction would not seriously affect the kinetics and rate constants observed in the present study, since for a given pressure and light intensity, it may be regarded, to a first approximation, simply as a constant factor reducing the extent of reaction 2.

A careful measurement of initial quantum yields of the mercury-photosensitized decompositions of the simple alkanes would be of obvious value in determining the exact nature of the primary process, and it is perhaps worth while to note briefly the conditions essential for such measurements as indicated by the present study. These are: (1) very low conversions, preferably 10 or 100 times lower than in the present work, in order to improve the accuracy of the extrapolation to zero time; (2) rigorous purification of hydrocarbons to eliminate trace amounts of unsaturates; and (3) low light intensities, sufficiently low to make reaction 10 negligible.

The author wishes to thank Miss M. Cooper and Miss M. Bilevicius, summer research assistants in 1957 and 1958 respectively, who performed some of the experimental work. The author also gratefully acknowledges tenure of a National Research Council of Canada postdoctoral fellowship.

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THE ABSOLUTE CONFIGURATION OF  
(+)-DES-(OXYMETHYLENE)-LYCOCTONINE HYDRIODIDE  
MONOHYDRATE AND (+)-DEMETHANOLACONINONE  
HYDRIODIDE TRIHYDRATE<sup>1</sup>

MARIA PRZYBYLSKA AND LÉO MARION

ABSTRACT

By X-ray analyses it has been possible to derive the absolute configuration of (+)-des-(oxymethylene)-lycoctonine and that of (+)-demethanolaconinone. These are shown in Figs. 2 and 3.

The detailed X-ray analyses of (+)-des-(oxymethylene)-lycoctonine hydriodide monohydrate (1) and (+)-demethanolaconinone hydriodide trihydrate (2) showed that these compounds have the same carbon-nitrogen ring structure (Fig. 1). The determinations of absolute configuration have since been carried out in order to establish whether the skeleton in Fig. 1 or its mirror image represents the ring structure of these compounds.

The principle on which it is possible to distinguish between optical isomers by means of X-rays in the case of anomalous dispersion was outlined by Bijvoet (3) and since then the absolute configuration of several compounds has been established (4, 5, 6).

The equi-inclination Weissenberg films were indexed taking into account the rotation of the crystal, the translation of the film, the position of the film, and the direction of the inclination of the camera (7). On the examination of Weissenberg films eight reflections corresponding to a right-handed set of axes were chosen for each compound and the intensities  $I_H$  and  $I_{\bar{H}}$  were estimated by visual comparison with an intensity strip. In each case the shortened and lengthened diffraction spots were measured and then averaged.

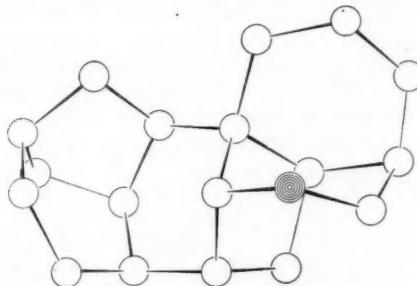


FIG. 1. The carbon-nitrogen skeleton of des-(oxymethylene)-lycoctonine and demethanolaconinone.

The intensities  $I_H = KF_H \cdot F_H^*$  and  $I_{\bar{H}} = KF_{\bar{H}} \cdot F_{\bar{H}}^*$  were calculated using the refined atomic co-ordinates obtained from the X-ray analyses. They corresponded to molecular models in right-handed sets of axes, the photographs of which were already published (1, 2). Their carbon-nitrogen skeleton is shown in Fig. 1. The contribution made by the hydrogen atoms was not taken into account, but it would certainly be small and considering large differences observed in intensities between  $I_H$  and  $I_{\bar{H}}$ , it could safely be neglected.

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The values for the real and imaginary dispersion corrections were those given by Dauben and Templeton (8). For the scattering factor for the iodine atom and  $\text{CuK}\alpha$  radiation they were  $\Delta f' = -1.1 \text{ e. \AA}^{-2}$  and  $\Delta f'' = 7.2 \text{ e. \AA}^{-2}$ .

(+)-Des-(oxymethylene)-lycoctonine Hydriodide Monohydrate

(+)-Des-(oxymethylene)-lycoctonine hydriodide monohydrate,  $\text{C}_{24}\text{H}_{39}\text{O}_6\text{N} \cdot \text{HI} \cdot \text{H}_2\text{O}$ , crystallizes in the space group  $P2_1$ . The authenticated sample was kindly provided by Dr. O. E. Edwards, who found the optical rotation of the anhydrous compound to be:  $[\alpha]_D^{28} +6 \pm 2^\circ$  ( $c$ , 1.0 in absolute ethanol). The  $b$  axis was taken as unique, polar axis and therefore the reflections which showed the violation of Friedel's law were  $hkl$  and  $h\bar{k}\bar{l}$  ( $I_{h\bar{k}\bar{l}} = I_{h\bar{k}\bar{l}}$ ). They were obtained by inclining the Weissenberg camera in opposite ways with respect to the X-ray beam. The films were exposed for identical periods of time and developed simultaneously. The crystal used was very small, roughly cylindrical in shape, about 0.06 mm in diameter, hence absorption corrections were not applied. The observed and calculated ratios of intensities are given in Table I.

TABLE I  
(+)-Des-(oxymethylene)-lycoctonine hydriodide monohydrate

$hkl$	$I_{hkl}/I_{\bar{k}\bar{l}}$ , calculated	$I_{hkl}/I_{\bar{k}\bar{l}}$ , observed
112	1.7	2.2
213	0.4	0.5
510	1.2	1.2
314	1.5	1.6
414	0.6	0.6
610	0.8	0.7
514	2.0	2.4
614	1.3	1.3

The agreement is satisfactory and it can be concluded that the molecular model used for calculation represents the absolute configuration of this compound. The structural formula emphasizing the diterpenoid character of the (+)-isomer is therefore as shown in Fig. 2. It should be noted that if the mirror image of that molecule was used for calculation, the ratio  $I_H/I_{\bar{H}}$  would be inverted.

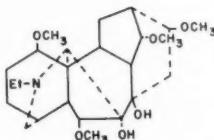


FIG. 2. (+)-Des-(oxymethylene)-lycoctonine.

(+)-Demethanolaconinone Hydriodide Trihydrate

The crystals of (+)-demethanolaconinone hydriodide trihydrate,  $\text{C}_{24}\text{H}_{45}\text{O}_8\text{N} \cdot \text{HI} \cdot 3\text{H}_2\text{O}$ , were prepared and authenticated by Dr. H. Mayer, who found the rotation was  $[\alpha]_D^{28} +59.2 \pm 1.5^\circ$  ( $c$ , 1.04 in water) (9). The space group of this compound is  $P2_12_12_1$ . The three axes of the unit cell are polar and therefore  $I_{hkl} = I_{h\bar{k}\bar{l}} = I_{h\bar{k}\bar{l}} = I_{\bar{h}\bar{k}\bar{l}}$ .

The crystal used was cylindrical in shape, about 0.12 mm in diameter, and the absorption corrections were not applied.

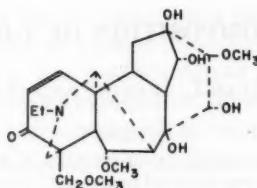


FIG. 3. (+)-Demethanolaconinone.

The results in Table II indicate that the (+)-isomer can be represented by the formula in Fig. 3 and its carbon-nitrogen skeleton by Fig. 1.

It is of interest to note that Dvornik and Edwards have concluded on molecular rotation grounds that the *Aconitum* alkaloid atisine (10) and the *Delphinium* alkaloid

TABLE II  
(+)-Demethanolaconinone hydriodide trihydrate

<i>hkl</i>	$I_{hkl}/I_{\bar{h}\bar{k}\bar{l}}$ , calculated	$I_{hkl}/I_{\bar{h}\bar{k}\bar{l}}$ , observed
511	1.8	2.2
513	0.5	0.5
611	0.4	0.3
2, 10, 2	0.4	0.3
751	3.0	3.5
821	5.7	3.2
822	1.6	1.5
912	0.6	0.7

ajaconine (11) also bear mirror image relationship to the common diterpenes. The biosynthesis of the lycocotonine family of alkaloids undoubtedly proceeds via intermediates with the atisine-type skeleton (12, 13) and the above correspondence of absolute configuration is in agreement with this.

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## THERMAL DECOMPOSITION OF 1-HEXANETHIOL<sup>1</sup>

PAUL E. GAGNON, JEAN L. BOIVIN,<sup>2</sup> AND DONALD C. WATSON<sup>3</sup>

### ABSTRACT

The uncatalyzed thermal decomposition of 1-hexanethiol was studied at temperature varying from 300 to 700° C and was observed to give 42% of olefinic hydrocarbons at 600° C. Dialkyl sulphides were also obtained at 550° C with a maximum yield of 13.3% at 650° C. The effect of sulphide catalyst was investigated and nickel sulphide was found to be the most effective: at low temperature (150–450° C) dihexylsulphide was produced and at higher temperature (450–600° C) olefinic hydrocarbons were obtained. Very little catalytic effect was observed with molybdenum and cadmium sulphides.

### INTRODUCTION

The thermal decomposition of aliphatic mercaptans has been extensively studied by several investigators (1 to 12), but it appears from the various results obtained that additional studies of this pyrolysis should be made in the absence or presence of catalysts at temperature of 150 to 750° C using 1-hexanethiol.

### EXPERIMENTAL

1-Hexanethiol was distilled and the fraction boiling at 153–154° C was used in the pyrolysis. Other materials had to be prepared for purpose of identification and analysis: dihexyl sulphide (13), dihexyl disulphide (14), and 1-hexene (15).

The apparatus used in the thermal decomposition of 1-hexanethiol was essentially the same as the one described in an earlier paper (12), together with the general procedure.

The liquid pyrolyzate was analyzed for mercaptan by the method of Kimball, Kramer, and Reid (16) and also by an amperometric method (17, 18) and for the olefinic material by an iodine method (19). Dialkyl sulphide was estimated by the bromide–bromate reagent (20), dialkyl disulphide by the Kolthoff method (21), and sulphur by a colorimetric method using sodium cyanide (22).

The gaseous pyrolyzate was analyzed by the Orsat apparatus (12).

For the uncatalyzed thermal decomposition, the pyrolysis tube was filled with Pyrex glass helices forming a column 40 cm high in the reaction zone; then 1-hexanethiol was dropped into the vaporizing flask at the rate of 0.5 g per minute. The liquid and gaseous pyrolyzates were analyzed and sampled for infrared measurements. Tables I and II show the composition of the liquid and gaseous products as a function of the temperature. Elemental sulphur could not be detected in the pyrolyzate residue until the pyrolysis temperature had risen to 500° C. At 550° C, the pyrolyzate contained 0.1% sulphur and only 0.3 at 650° C.

In the metal sulphide catalyzed decompositions, the pyrolysis tube was packed as follows: a 2-cm-thick plug of glass wool was placed in the pyrolysis tube at the lower end of the decomposition zone. A 3-cm layer of 8-mm glass helices was placed on top of the plug, followed by a 3-cm layer of the metal sulphide catalyst. The placing of alternate layers of glass helices and catalyst was continued until a column 40 cm high was built up

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in the decomposition tube. This type of packing was used in preference to a solid column of metal sulphide catalyst in order to prevent channeling and hence loss of catalyst contact of the vaporized mercaptan. The results obtained are shown in Tables I and II for the composition of liquid and gaseous pyrolyzates. With the sulphide catalysts, elemental sulphur was not detected in pyrolyzate liquids at temperatures below 400° C. At a decomposition temperature of 550° C, the sulphur content was only 0.1% with NiS and 0.2 with MoS<sub>3</sub> and CdS.

TABLE I  
Liquid products of 1-hexanethiol decomposition

Catalyst	Temp., °C.	Liquid recovery, %	Percentage composition of liquid products			
			Mercaptan	Olefin	Sulphide	Disulphide
Nil	300	90.7	100.0	—	—	—
	350	90.6	100.0	—	—	—
	400	88.4	100.0	—	—	—
	450	87.3	94.5	0.7	0.0	0.2
	500	77.5	87.7	8.9	0.0	1.8
	550	61.0	57.8	27.4	0.1	2.5
	600	25.4	15.3	42.3	8.1	2.5
	650	11.9	0.0	27.0	13.5	2.7
NiS	700	6.8	0.0	18.5	0.1	2.7
	200	86.9	71.1	0.0	21.5	0.0
	250	85.8	20.9	0.0	35.2	0.0
	300	83.5	17.7	2.3	34.0	0.0
	350	72.2	29.2	10.4	25.4	0.0
	400	64.1	44.0	16.9	12.2	3.0
	450	58.9	57.0	23.0	0.0	9.5
	500	45.7	48.2	26.2	0.0	16.1
MoS <sub>3</sub>	550	32.8	21.0	17.7	0.0	14.0
	600	14.8	0.0	5.4	0.0	12.8
	300	82.6	89.0	3.2	0.3	0.0
	350	78.4	66.2	6.2	9.3	1.3
	400	74.6	40.7	9.1	12.8	4.8
	450	70.6	30.7	19.1	15.4	6.9
	500	65.3	15.8	28.0	28.7	7.0
	550	40.7	13.2	24.4	32.6	9.0
CdS	600	12.4	0.0	22.2	34.0	12.8
	300	87.6	85.2	1.0	0.0	0.0
	350	82.6	68.2	4.8	2.3	0.0
	400	78.2	52.0	9.8	10.7	1.3
	450	66.7	40.8	18.7	17.3	2.4
	500	38.5	27.6	29.2	27.4	3.6
	550	29.6	14.0	22.6	26.6	13.0
	600	17.4	0.0	6.7	20.0	16.2

#### DISCUSSION

There is a general agreement that the thermal decomposition of an aliphatic mercaptan will result in the formation of a dialkyl sulphide and an unsaturated hydrocarbon. Several investigators (1, 2, 12) have pointed out that at a high decomposition temperature, the mercaptan undergoes loss of hydrogen sulphide, which results in the formation of an unsaturated hydrocarbon as the main product. At a lower decomposition temperature, there is only partial desulphurization, and a dialkyl sulphide is the major product formed. As a result of the present investigation, this generalization has been found to be true only under certain conditions.

In the thermal decomposition of 1-hexanethiol without catalyst, it was found that unsaturated hydrocarbons were produced at lower temperatures than the dialkyl

TABLE II  
Gaseous products of 1-hexanethiol decomposition

Catalyst	Temp., °C	Gas produced, % by weight	Percentage composition of gaseous products			
			Hydrogen sulphide	Olefin	Hydrogen	Residual
Nil	450	4.7	90.0	0.0	0.0	10.0
	500	14.5	79.8	7.0	0.4	12.8
	550	31.0	61.2	18.5	2.4	17.9
	600	66.6	44.0	27.1	2.7	26.2
	650	80.1	33.4	27.8	2.9	36.2
	700	85.2	30.1	26.1	2.2	41.4
NiS	350	13.5	81.2	0.4	0.4	18.0
	400	21.6	70.0	5.6	6.1	18.3
	450	26.8	56.8	9.2	10.2	23.8
	500	40.0	46.2	14.8	13.4	25.6
	550	52.9	30.6	26.4	11.8	31.2
	600	70.9	20.2	34.8	2.8	42.2
MoS <sub>2</sub>	350	11.2	87.5	0.1	0.0	12.4
	400	15.2	83.3	3.9	1.3	11.8
	450	20.5	80.0	9.7	3.8	6.5
	500	45.1	71.2	15.8	6.8	6.2
	550	73.4	49.8	21.2	6.4	22.6
	600	82.6	14.4	26.1	7.3	52.2
CdS	400	11.8	78.6	1.3	1.6	18.5
	450	23.3	75.0	8.0	5.2	11.8
	500	51.5	50.8	15.2	6.3	27.7
	550	60.4	36.0	22.6	6.5	34.9
	600	72.6	25.2	28.1	6.8	39.9

sulphides. Olefinic hydrocarbons were first detected at 450° C, and reached a maximum concentration of 42.3% at a decomposition temperature of 600° C. On the other hand, dihexyl sulphide was not formed until 550° C, and the maximum content of 8.1% was obtained at a decomposition temperature of 600° C.

These observations were not found true of the subsequent catalytic studies. With nickel sulphide as catalyst, dialkyl sulphide formation began as low as 200° C and increased to give a maximum pyrolyzate concentration of over 35% at 250° C to 300° C, the temperature range at which olefinic hydrocarbon formation began. In the case of the molybdenum and cadmium sulphide catalysts, analysis of the liquid residues indicated that sulphide and unsaturated hydrocarbons were both formed at the same decomposition temperature range, i.e., between 300 and 350° C.

It then appears that in non-catalytic decompositions, unsaturated hydrocarbons are produced at a lower temperature than the dialkyl sulphides. A very active catalyst like nickel sulphide reverses this, causing sulphides to be produced at the lower temperature. Molybdenum and cadmium sulphides, on the same basis, are classed as possessing only moderate catalytic activity, in that sulphides and olefins are produced at the same temperature.

The effect of the catalyst on the decomposition of 1-hexanethiol is also indicated by the residual thiol content of the liquid samples. As noted from the analytical results, 1-hexanethiol undergoes marked decomposition without catalyst in a very narrow temperature range of 100° C, i.e., between 500 and 600° C. In the studies with nickel sulphide, decomposition took place in two stages. The first decomposition, which was accompanied by considerable sulphide formation, was determined as catalytic, extending from 150 to

450° C. The second stage was determined to be thermal, extending from 450 to 600° C. However, in molybdenum and cadmium sulphide decompositions, thiol decomposition is considered as a one-stage process, due mainly to a thermal effect. The decomposition range extended over a much wider temperature zone, from about 300 to 600° C.

Similar conclusions regarding the activities of the different catalysts were indicated from dialkyl disulphide formation. During the non-catalytic decompositions, very little disulphide was produced. The disulphide content did not rise above 3% of the total pyrolyzate, and therefore could not be considered as a major decomposition product. However, in nickel sulphide decomposition studies, disulphide was formed in moderate quantities in the 450 to 600° C temperature range. With the sulphides of molybdenum and cadmium, the disulphide content accounted for over 10% of the total only in the final 50° C decomposition range studied, i.e., from 550 to 600° C.

From the analytical results, it should be noted that there were a number of liquid and gaseous samples obtained during the pyrolysis of 1-hexanethiol, in which the known components, analyzed by chemical means, constituted less than 75% of the total sample weight. In most cases, these were obtained from high temperature decomposition studies, both with and without catalyst. Infrared analysis indicated the formation of many decomposition products containing less than six carbon atoms. These smaller fragments included the saturated hydrocarbon gases, methane, ethane, propane, and butane, as well as the olefinic hydrocarbons, ethylene, propylene, and butylene. A number of sulphur-containing compounds such as thiophene and carbon disulphide were also identified by infrared examination.

The formation of hydrogen sulphide could be considered as a function of carbon-sulphur cleavage whereas gaseous hydrocarbon formation would indicate carbon-carbon cleavage. The relative quantities of these two components in any given sample indicated the major point of cleavage at a particular decomposition temperature. In non-catalytic pyrolysis, hydrogen sulphide was produced at 450° C, and remained the main gaseous component until a temperature of 600° C had been reached. In the 600 to 700° C range, hydrocarbons formed the greater part of the effluent gas, indicating that the above 600° C cleavage of the carbon chain occurred more readily than that of the carbon-sulphur bond. From the results of gas analysis with the sulphide catalysts, the same generalization holds true, with the exception that lower temperatures were required. Hydrogen sulphide was produced at about 350° C and carbon-carbon cleavage did not become the predominant reaction until a decomposition temperature of 500° C had been reached.

One final difference between catalytic and non-catalytic decomposition was indicated by the hydrogen content of the effluent gas. In non-catalytic decomposition, less than 3% hydrogen was produced throughout the temperature range studied. Sulphide catalysts, however, gave an increased hydrogen content of the effluent gas. With nickel sulphide, 15% hydrogen was produced at 500° C; approximately half this quantity was obtained with molybdenum and cadmium sulphide catalysts.

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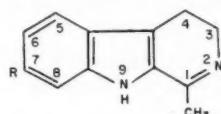
# A SYNTHESIS OF HARMALINE<sup>1</sup>

IAN D. SPENSER

## ABSTRACT

The synthesis of 1-methyl-3,4-dihydro- $\beta$ -carboline (harmalan) and of two of its derivatives by dehydration of the corresponding 1-hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carbolines is described. Harmalan was also obtained by oxidative decarboxylation of 1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline-1-carboxylic acid.

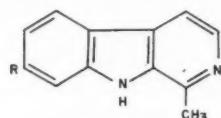
Harmalol (I), isolated from *Peganum harmala* L. (1), and the corresponding methyl ether harmaline (II), obtained from the same plant (1), as well as from *Banisteria caapi* Spruce (2), are the only 3,4-dihydro- $\beta$ -carboline derivatives hitherto found to occur in nature. All other naturally occurring compounds containing the  $\beta$ -carboline ring system are either fully aromatic (IV) or contain a 1,2,3,4-tetrahydro-structure (VI) (3a). Amongst the structurally analogous isoquinoline alkaloids only two, psychotrine and O-methyl-psychotrine (3b) have so far been recognized as 3,4-dihydro-derivatives. The 3,4-dihydro-structure thus represents a rare oxidation state in these plant bases.



I R = OH



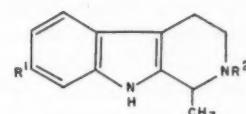
II R = OCH<sub>3</sub>



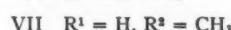
IV R = H



V R = OCH<sub>3</sub>



VI R<sup>1</sup> = R<sup>2</sup> = H



VII R<sup>1</sup> = H, R<sup>2</sup> = CH<sub>3</sub>



VIII R<sup>1</sup> = OCH<sub>3</sub>, R<sup>2</sup> = H

Although the biosynthesis of the  $\beta$ -carboline alkaloids has not so far been investigated, it has long been assumed (4) that the nucleus arises in the plant by a Mannich-type condensation of tryptamine or oxytryptamine with an aldehyde to yield a tetrahydro- $\beta$ -carboline derivative. Such condensations have been carried out in vitro under mild conditions of temperature and pH (e.g. (5)), and a number of tetrahydro- $\beta$ -carbolines have been found in plants (e.g. 1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline (eleagnine) (VI) (6, 7, 8), 1,2-dimethyl-1,2,3,4-tetrahydro- $\beta$ -carboline (leptocladine) (VII) (9), and 1-methyl-7-methoxy-1,2,3,4-tetrahydro- $\beta$ -carboline (tetrahydroharmine) (VIII) (2, 8)).

Partial dehydrogenation of these tetrahydro-derivatives has been postulated (4, 7, 10) to account for the origin of the dihydro-derivatives harmaline (II) and harmalol (I), and further loss of hydrogen for that of the  $\beta$ -carbolines (e.g. 1-methyl- $\beta$ -carboline (harman) (IV) (3a) and its 7-methoxy-derivative (harmine) (V) (3a)).

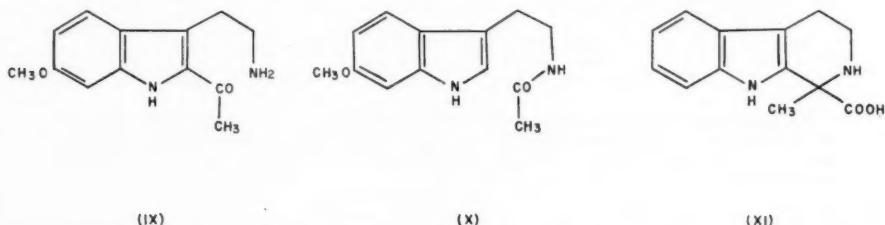
If this stepwise oxidation sequence were indeed to represent the biosynthetic origin of dihydro- $\beta$ -carbolines and  $\beta$ -carbolines, the former might be expected to accompany the latter frequently in the plant. The comparative rarity of the dihydro-derivatives is thus puzzling and led us to consider other possible biogenetic routes.

Neither of the reported syntheses of harmaline (II) can be regarded as models for in vivo formation. The synthetic base was first obtained (11) by cyclization of 1-acetyl-2-

<sup>1</sup>Manuscript received July 2, 1959.

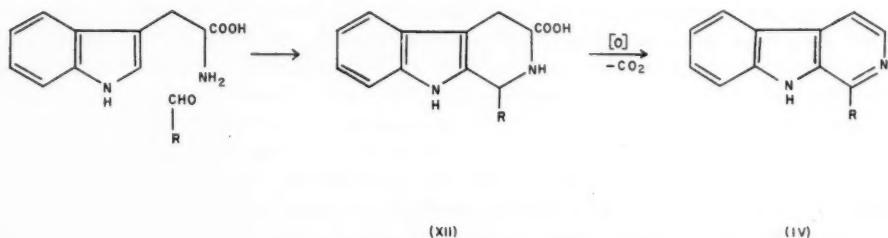
Contribution from the Department of Chemistry, McMaster University, Hamilton, Ontario.

aminoethyl-6-methoxyindole (IX), and later by Bischler-Napieralski ring closure of



$N_{\beta}$ -acetyl-6-methoxytryptamine (X) (12). Much earlier Perkin and Robinson (4) had obtained the compound by oxidation of tetrahydroharmine (VIII) with permanganate in acetone. Under nonacidic conditions dihydro- $\beta$ -carbolines thus appear to be stable to oxidizing agents. This stability has now been confirmed: 1-methyl-3,4-dihydro- $\beta$ -carboline (III) (harmalan) was obtained in good yield both by oxidation of 1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline (VI) (13) in acetone with permanganate, and also by oxidative decarboxylation of 1-methyl-1,2,3,4-tetrahydro- $\beta$ -carboline-1-carboxylic acid (XI) (5) with silver oxide in aqueous solution. This latter synthesis of a dihydro- $\beta$ -carboline was modelled on our studies of oxidative decarboxylation of amino acids (14).

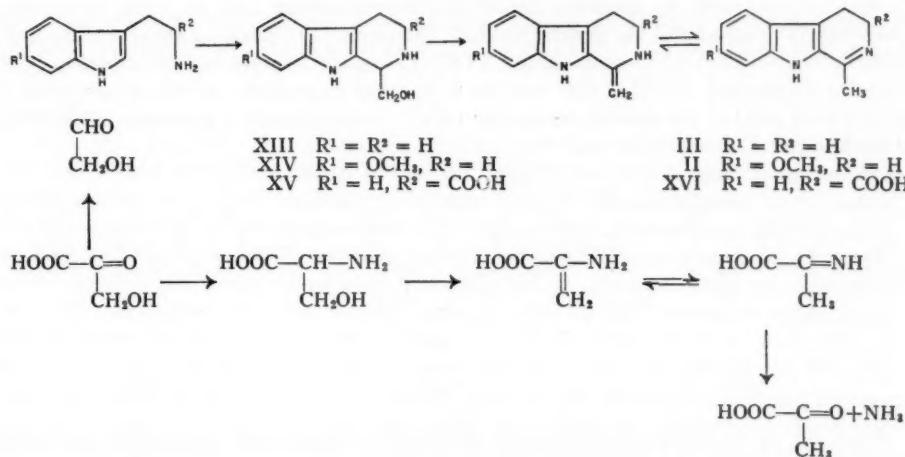
Under acid conditions (nitric acid (15), chromic acid (16), acid permanganate (12, 17)) dihydro- $\beta$ -carbolines are oxidized to  $\beta$ -carbolines. Oxidation of tetrahydro- $\beta$ -carbolines under similar conditions does not take place as readily (12) and leads to  $\beta$ -carbolines in poor yield (18).  $\beta$ -Carbolines are obtained in good yield by acid dichromate oxidation of tetrahydro- $\beta$ -carboline-3-carboxylic acids (XII), decarboxylation accompanying the reaction (19). The biogenetic origin of  $\beta$ -carbolines, without intermediate formation of dihydro- $\beta$ -carbolines, has been proposed in analogy to this reaction sequence (20).



In the present synthesis harmaline was obtained in two physiologically possible steps, the C=N double bond being introduced by dehydration, rather than oxidatively: 6-Methoxytryptamine (21)<sup>2</sup> was condensed with glycolaldehyde to give ( $\pm$ )-1-hydroxymethyl-7-methoxy-1,2,3,4-tetrahydro- $\beta$ -carboline (XIV) in good yield. This step involves the usual Mannich reaction between a biogenetic amine and an aldehyde. The latter, glycolaldehyde, is known to arise enzymically *inter alia* by decarboxylation of hydroxypyruvic acid (22), a metabolic precursor of serine (23).

In a similar manner tryptamine gave ( $\pm$ )-1-hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline (XIII), and *dl*-tryptophan yielded the corresponding 3-carboxylic acid (XV) (24).

<sup>2</sup>I am grateful to Dr. R. A. Abramovitch, University of Saskatchewan, for a specimen of this material.



Dehydration of these tetrahydro-derivatives gave the corresponding 3,4-dihydro- $\beta$ -carbolines. Harmaline (II) was obtained in 70% yield with 90% w/w phosphoric acid, harmalan (III) in 75% yield with phosphoric acid and in 25% yield with 50% w/v sulphuric acid. In each instance the product was indistinguishable from an authentic specimen.<sup>3</sup> 1-Methyl-3,4-dihydro- $\beta$ -carboline-3-carboxylic acid (XVI) was obtained in moderate yield with 50% w/v sulphuric acid. The course of the dehydration reaction was followed in each case by observing the change in ultraviolet absorption (Figs. 1 and 2).

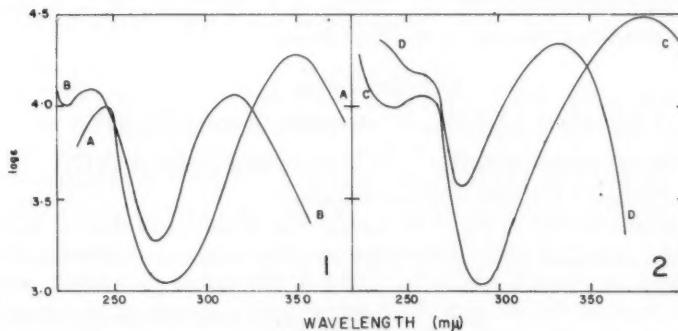


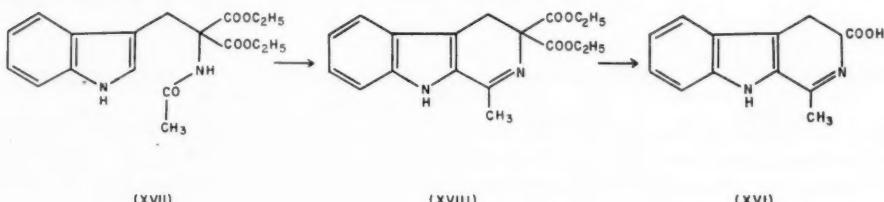
FIG. 1. 1-Methyl-3,4-dihydro- $\beta$ -carboline (harmalan). Curve A, in 0.1 N HCl in aqueous ethanol; curve B, in 0.1 N NaOH in aqueous ethanol.

FIG. 2. 1-Methyl-7-methoxy-3,4-dihydro- $\beta$ -carboline (harmaline). Curve C, in 0.1 N HCl in aqueous ethanol; curve D, in 0.1 N NaOH in aqueous ethanol.

The dihydro- $\beta$ -carboline (XVI) derived from tryptophan had not hitherto been described. Another synthetic route was therefore sought to confirm its identity. Bischler-Napieralski ring closure of  $N_{\beta}$ -acetyltryptophan was not suitable since it has proved unsuccessful with classical dehydrating agents (24, 25) while with polyphosphoric acid

<sup>3</sup>I am greatly indebted to Dr. T. M. Sharp, Wellcome Laboratories, London, England, for a sample of natural harmaline.

it was accompanied by decarboxylation and aromatization (26) to yield 1-methyl- $\beta$ -carboline (IV) instead of the desired product. However, cyclization of ethyl  $\alpha$ -acetamido- $\alpha$ -carbethoxy- $\beta$ -(3-indolyl)-propionate (XVII) (27) gave 1-methyl-3,3-dicarbethoxy-3,4-dihydro- $\beta$ -carboline (XVIII) (28) and the latter was saponified and decarboxylated, to give a 65% yield of the desired compound (XVI), identical with a specimen obtained by dehydronation.



A second, as yet unidentified material, differing in infrared and ultraviolet absorption from the main product was also isolated in this reaction.

The dehydration step in the present harmaline synthesis parallels the catabolic pathway of serine (29), enzymatic dehydration to  $\alpha$ -aminoacrylic acid, and rearrangement to  $\alpha$ -iminopropionic acid. Whereas this compound spontaneously hydrolyzes to pyruvic acid and ammonia, the imino-linkage in harmaline is stabilized by conjugation with the indole system. In vitro this dehydration of serine requires strong acid (30).

The synthesis of harmaline here described is put forward as a possible biogenetic route and an alternative to the oxidative pathway postulated by earlier authors (4, 7, 10). The recent confirmation (31) of the structure of calycotomine as 1-hydroxymethyl-6,7-dimethoxy-1,2,3,4-tetrahydroisoquinoline, analogous to the intermediate in the present synthesis, lends additional interest to this hypothesis.

## EXPERIMENTAL

### 1-METHYL-3,4-DIHYDRO- $\beta$ -CARBOLINE (HARMALAN) (III)

(1) By Dehydration of 1-Hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline (XIII)

( $\pm$ )-1-Hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline

Tryptamine hydrochloride (5.9 g, 0.03 moles) was dissolved in 250 ml warm water containing 15 ml 2 N HCl (1.095 g, 0.03 moles) and the solution was filtered. To the cold solution was added an aqueous solution of 1.90 g (0.032 moles) glycolaldehyde (32) and the mixture was kept on the steam bath (2 hours) until a sample no longer gave a precipitate with dinitrophenylhydrazine. The cooled solution was then treated with charcoal, filtered, extracted with ether to remove nonbasic impurities, concentrated, and treated with excess of 20% NaOH, when the product precipitated as an oil which crystallized on standing. It was taken up in ether, and the solution was dried with KOH and concentrated to yield an oil which crystallized on digestion with warm water to give the trihydrate of 1-hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline (6.25 g, 81%) melting at 138–139° after sintering below 100°. Recrystallization from aqueous ethanol did not raise the melting point. Distillation of a small sample at 2.10<sup>–2</sup> mm and 140–150° gave an oil, crystallizing into a white solid, melting at 144–145°, which still retained water of crystallization. (Found: H<sub>2</sub>O, 19.18. C<sub>12</sub>H<sub>14</sub>ON<sub>2</sub>·3H<sub>2</sub>O requires H<sub>2</sub>O, 21.10%. After drying at 120° found: C, 71.5; H, 6.8. C<sub>12</sub>H<sub>14</sub>ON<sub>2</sub> requires C, 71.5; H, 7.0%.)

The hydrochloride, recrystallized from ethanol, melted at 215–216° after darkening from 205°. (Found: C, 56.3; H, 6.8; N, 10.5.  $C_{12}H_{15}ON_2Cl, H_2O$  requires C, 56.1; H, 6.7; N, 10.9%).

#### *Harmalan*

(i) 90% *w/w*  $H_3PO_4$ .—The above tetrahydro- $\beta$ -carboline trihydrate (3.37 g, 0.013 moles) was wetted with 10 ml water, 100 ml 90%  $H_3PO_4$  was added, and the suspension was kept on the steam bath until the absorption band at 280 m $\mu$ , characteristic of the indole chromophore of the starting material, had disappeared. The reaction was complete after 2 hours. The dark brown solution was diluted with water, extracted with ether, treated with charcoal, and made alkaline with 20% NaOH. The precipitate was collected, dried in air, and extracted in the Soxhlet extractor with 70–100° petroleum ether, from which harmalan crystallized in fluffy needles, melting at 178–179° in a total yield of 1.80 g (75%). For analysis a sample was sublimed at 1.10<sup>-3</sup> mm and 90° C. (Found: C, 77.9; H, 6.4; N, 15.1. Calc. for  $C_{12}H_{12}N_2$ : C, 78.2; H, 6.6; N, 15.2%). Infrared absorption (Nujol) (cm<sup>-1</sup>): 1622 (m), 1605 (m), 1570 (m), 1550 (s). Ultraviolet absorption (Fig. 1) ( $\lambda_{max}$ , m $\mu$  (log  $\epsilon$ )); in 0.1 N HCl: 245 (4.04); 350 (4.28); in 0.1 N NaOH: 240 (4.09), 315 (4.06).

(ii) 50% *w/v*  $H_2SO_4$ .—The tetrahydro- $\beta$ -carboline (0.11 g, 0.00043 moles) was treated with an ice-cold mixture of 2 ml 95%  $H_2SO_4$  and 4 ml water. After 2 hours on the steam bath and standing overnight, the solution showed a strong dihydro- $\beta$ -carboline peak at 350 m $\mu$ , but the indole peak at 280 m $\mu$  was still apparent. The latter had disappeared after a further 2 hours on the steam bath with an additional 1 ml of 95%  $H_2SO_4$ . The solution was diluted with water, treated with charcoal, and the product precipitated by addition of a little 20% NaOH, when harmalan, melting at 176–177°, was obtained in poor yield (25%). When the experiment was carried out at room temperature, even after 1 week unchanged starting material was recovered.

(2) *By Oxidation of 1-Methyl-tetrahydro- $\beta$ -carboline (VI)*

1-Methyl-1,2,3,4-tetrahydro- $\beta$ -carboline (13) (0.186 g, 0.001 moles) was dissolved in acetone. To the ice-cold solution was added 0.11 g (0.0007 moles) powdered  $KMnO_4$ . When reaction was complete,  $MnO_2$  was filtered off, the solution evaporated, the residue taken up in ether, dried over NaOH, the solvent removed, and the residual solid extracted with boiling ligroin, from which harmalan (0.11 g, 65%), melting at 176–178°, crystallized.

(3) *By Oxidative Decarboxylation of 1-Methyl-1,2,3,4-tetrahydro- $\beta$ -carboline-1-carboxylic Acid (XI)*

#### *1-Methyl-1,2,3,4-tetrahydro- $\beta$ -carboline-1-carboxylic Acid*

Cooled aqueous solutions of tryptamine hydrochloride (0.98 g, 0.005 moles) and pyruvic acid (0.48 g, 0.0055 moles) were mixed and left at 37° overnight when the product had separated in 85% yield (0.96 g) as colorless crystals, melting with decarboxylation at 217–219°. Recrystallization from dilute aqueous ammonia did not raise the melting point, which is reported as 220° (5).

#### *Harmalan*

The above amino acid (0.115 g, 0.0005 moles) in 20 ml water was refluxed 24 hours with freshly precipitated  $Ag_2O$  (0.23 g, 0.001 moles). Metallic silver deposited, and the solution gave an ultraviolet absorption curve characteristic of a dihydro- $\beta$ -carboline. The mixture was filtered hot. On cooling a solid precipitated, which on recrystallization from boiling petroleum ether gave 0.079 g (85%) of harmalan, melting at 178–180°.

The products obtained from each of the above experiments were compared with a sample of harmalan prepared from  $N_{\beta}$ -acetyltryptamine (12) and were found to have identical ultraviolet (Fig. 1) and infrared (Nujol) spectra, melting points, and mixed melting points.

### 1-METHYL-7-METHOXY-3,4-DIHYDRO- $\beta$ -CARBOLINE (HARMALINE) (II)

6-Methoxytryptamine (21) (0.033 g, 0.00017 moles) was dissolved in 3.5 ml 0.1 *N* HCl (0.00035 moles) and heated on the steam bath with 0.011 g (0.00019 moles) glycolaldehyde, until a sample no longer gave a precipitate with dinitrophenylhydrazine (1½ hours). The solution was filtered, concentrated, washed into a continuous extractor, overlaid with ether, and made alkaline with 10 ml 0.5 *N* NaOH. Eighteen hours' extraction, drying over KOH and removal of solvent, gave 50 mg of a white crystalline solid, melting at 170–175°, after sintering at 85°, presumably a hydrate of 1-hydroxymethyl-7-methoxy-1,2,3,4-tetrahydro- $\beta$ -carboline (XIV). (Ultraviolet absorption ( $\lambda_{\text{max}}$ ,  $m\mu$  (log  $\epsilon$ )): 225 (4.37), 275 (3.53), 295 (3.65) in ethanol.) Without further purification, this base was treated with 2.5 ml 90%  $H_3PO_4$  and kept on the steam bath for 2 hours, when the solution gave an ultraviolet curve identical with that of natural harmaline (footnote 2). The solution was diluted with water, placed in a continuous extractor, made alkaline with 20% NaOH, and the product was extracted into ether. The ether extract was dried, the solvent removed, and the product distilled at 10<sup>-3</sup> mm and 120–140° to yield 27 mg (72%) harmaline, melting at 235–237°, identical with an authentic specimen in infrared and ultraviolet absorption (Fig. 2),  $R_f$  value (0.89) in 95% ethanol/.880 ammonia (99:1), melting point and mixed melting point. (Found: C, 72.6; H, 6.6; N, 13.1. Calc. for  $C_{13}H_{14}ON_2$ : C, 72.8; H, 6.6; N, 13.1%). Infrared absorption in (Nujol) ( $\text{cm}^{-1}$ ): 1620 (s), 1600 (m), 1570 (m), 1535 (s). Ultraviolet absorption (Fig. 2) ( $\lambda_{\text{max}}$ ,  $m\mu$  (log  $\epsilon$ )): in 0.1 *N* HCl: 260 (4.07), 380 (4.49); in 0.1 *N* NaOH: 260 (4.18) (shoulder), 335 (4.34).

A portion was converted to the picrate, orange needles, melting at 228–229° after sintering at 215°, after recrystallization from aqueous ethanol, identical with the picrate derived from the authentic sample.

### 1-METHYL-3,4-DIHYDRO- $\beta$ -CARBOLINE-3-CARBOXYLIC ACID (XVI)

#### (1) By Dehydration of 1-Hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline-3-carboxylic Acid (XV)

##### 1-Hydroxymethyl-1,2,3,4-tetrahydro- $\beta$ -carboline-3-carboxylic Acid

*dl*-Tryptophan (1.02 g, 0.005 moles) was dissolved in *N* HCl (5 ml, 0.005 moles), 0.33 g glycolaldehyde (0.0055 moles) was added, and the mixture was kept on the steam bath for 2 hours when a sample no longer gave a precipitate with dinitrophenylhydrazine. The dark solution was treated with charcoal, the pH of the filtrate was adjusted to pH 7, and a small amount of precipitate was removed by filtration. On concentration the product crystallized, and on recrystallization from boiling water was obtained in 51% yield (0.63 g) as long needles, decomposition 256–257° after darkening from 235°. No attempt was made to separate the diastereoisomers. A melting point of 234° was reported (24) for the product derived from *l*-tryptophan. (Found: C, 63.1; H, 5.7; N, 11.6. Calc. for  $C_{13}H_{14}O_3N_2$ : C, 63.4; H, 5.7; N, 11.4%).

##### 1-Methyl-3,4-dihydro- $\beta$ -carboline-3-carboxylic Acid

The above amino acid (0.37 g, 0.0015 moles) was treated with an ice-cold solution of 2 ml 95%  $H_2SO_4$  in 5 ml  $H_2O$ . After keeping this solution at room temperature for 48 hours no absorption at 355  $m\mu$  was observed. The solution was then kept on the steam bath for

2 hours, when absorption at 355 m $\mu$  appeared, but since the ultraviolet absorption band at 280 m $\mu$  was still strong, a further 1 ml 95% H<sub>2</sub>SO<sub>4</sub> was added. After 2 hours the reaction was complete. The solution was diluted with water, absorbed on a Zeocarb cation exchange resin in the acid form, and eluted with ammonia. The eluate was concentrated and the residue taken up in aqueous ethanol, treated with charcoal and allowed to stand at 0°, giving 88 mg (26%) of yellow crystals, melting at 189–190° after darkening at 185°, of the dihydrate of 1-methyl-3,4-dihydro- $\beta$ -carboline-3-carboxylic acid. (Found: H<sub>2</sub>O, 14.0. C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub>·2H<sub>2</sub>O requires H<sub>2</sub>O, 13.6%.) After drying at 100° found: C, 68.2; H, 5.4; N, 12.0. C<sub>12</sub>H<sub>12</sub>O<sub>2</sub>N<sub>2</sub> requires C, 68.4; H, 5.3; N, 12.3%.) Infrared absorption (Nujol) (cm<sup>-1</sup>): 1655 (m), 1632 (m), 1615 (m), 1592 (s), 1570 (s), 1523 (m), 1445 (s). Ultraviolet absorption ( $\lambda_{\text{max}}$ , m $\mu$  (log  $\epsilon$ )): in 0.1 N HCl: 245 (3.97), 355 (4.29); in 0.1 N NaOH: 235 (4.10), 315 (4.07).

(2) *By Malonic Ester Synthesis*

*Ethyl  $\alpha$ -Acetamido- $\alpha$ -carbethoxy- $\beta$ -(3-indolyl)-propionate (XVII)*

This was prepared by the pyridine method of Howe, Zambito, Snyder, and Tishler (27) which was found more satisfactory than their other methods. It was obtained as colorless crystals, melting at 142–144°.

*1-Methyl-3,3-dicarbethoxy-3,4-dihydro- $\beta$ -carboline (XVIII) (cf. (28))*

Ethyl  $\alpha$ -acetamido- $\alpha$ -carbethoxy- $\beta$ -(3-indolyl)-propionate (1.04 g, 0.003 moles) was gently warmed with 5 ml POCl<sub>3</sub> for 45 minutes, when the band at 280 m $\mu$  in the ultraviolet spectrum of the original solution had been completely replaced by the band at 355 m $\mu$ . The reaction mixture had become dark brown. Excess POCl<sub>3</sub> was distilled off at room temperature at 10<sup>-3</sup> mm, and the brown tarry residue triturated with excess NH<sub>3</sub>. On standing overnight the tarry salt had been converted into the solid, crude base, which was filtered off and taken up in ether. The ether solution was washed with dilute NH<sub>3</sub> and H<sub>2</sub>O, and the product then extracted into 0.02 N HCl. The acid solution was immediately treated with dilute ammonia, and the product re-extracted into ether and dried over Na<sub>2</sub>SO<sub>4</sub>. Removal of solvent gave a yellow solid which was dissolved in acetone. Addition of 70–100° petroleum ether and cooling gave the product as long yellow needles, melting at 154–156°, which was identical in infrared and ultraviolet absorption with the product described by Hardegger and Corrodi (28), melting at 147–149° (yield 0.45 g, 44%). (Found: C, 65.6; H, 6.3; N, 8.7. Calc. for C<sub>18</sub>H<sub>20</sub>O<sub>4</sub>N<sub>2</sub>: C, 65.8; H, 6.1; N, 8.5%.) Infrared absorption (cm<sup>-1</sup>) 1725 (s), 1612 (w), 1595 (m), 1570 (w), 1540 (m), 1500 (w). Ultraviolet absorption ( $\lambda_{\text{max}}$ , m $\mu$  (log  $\epsilon$ )): in 0.1 N HCl: 245 (4.11), 355 (4.40); in 0.1 N NaOH: 240 (4.18), 318 (4.22).

*1-Methyl-3,4-dihydro- $\beta$ -carboline-3-carboxylic Acid*

1-Methyl-3,3-dicarbethoxy-3,4-dihydro- $\beta$ -carboline (0.2 g, 0.00061 moles) was wetted with a little ethanol, suspended in 1.22 ml N NaOH (0.00122 moles), and warmed for 2 hours. A small quantity of tarry material was filtered off and the filtrate acidified by addition of 19 ml 0.982 N HCl (0.00183 moles) and decarboxylation accelerated by keeping the mixture on a steam bath for 30 minutes. A small amount of solid was filtered off. The solution was applied to a column of Dowex 50, was washed free of chloride ion, and the product eluted with M NH<sub>3</sub>. Concentration gave a small amount of a substance, crystallizing as long needles and melting at 188–190°, which gave an infrared spectrum ((Nujol) (cm<sup>-1</sup>): 1620 (m), 1545 (m), 1510 (w)) different from that of the expected product (*vide supra*) and an ultraviolet absorption which even after repeated recrystallization of

\*I thank Dr. E. Hardegger for a reference sample of this material.

the substance showed, in addition to the dihydro- $\beta$ -carboline bands at 245 m $\mu$  and 355 m $\mu$  in acid solution and 240 m $\mu$  and 318 m $\mu$  in alkaline solution, another band at 278 m $\mu$  in acid solution and at 256 m $\mu$  (shoulder) in alkaline solution.

Further concentration of the solution gave the desired product (0.09 g, 64%) as yellow crystals, melting at 186–188°, identical in infrared (Nujol) and ultraviolet absorption (*vide supra*), melting point, and mixed melting point with that obtained by dehydration.

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## PHYSICAL PROPERTIES OF ALKYL PYRROLES AND THEIR SALTS<sup>1</sup>

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### ABSTRACT

The structures of the ions formed by several alkyl pyrroles in hydrochloric acid are deduced from proton resonance spectra. Basicity values for three alkyl pyrroles are determined from ultraviolet spectra of their salts in buffer solutions. An attempt is made to estimate the basicity of other pyrroles from the variation of the —OD stretching frequency of methanol-*d* in solution in the pyrroles. Variations of the free and bonded NH frequencies of alkyl pyrroles are shown to be a simple function of the positions and number of the substituents.

### INTRODUCTION

The basic nature of substituted pyrroles has been emphasized recently (1, 2, 3, 4, 5) and suggestions made about the structures of the protonated forms (3, 4, 5, 6). Proton magnetic resonance seemed to present a good method for defining these structures, which are probably the activated forms of pyrroles in acid (3, 4, 6).

The proton magnetic resonance spectra of pyrrole and some substituted pyrroles have been given in a previous publication (12) and the frequencies completely assigned. The spectra of the methyl-substituted pyrroles given here can be interpreted on the same basis and need not be discussed in detail. However, the pyrrole hydrochlorides give much more complex spectra and these will be discussed here. The striking differences between the spectra of the hydrochlorides and of the parent compounds show immediately that the methyl pyrroles in acid solution do not form merely loose addition complexes, but true salts, and the structure of the cations can be found from the interpretation of the proton magnetic resonance spectra.

Basicity constants for two substituted pyrroles have been reported (5) and in addition to a redetermination of these values, two further pyrroles have been examined. Since the application of the ultraviolet method is very limited (by instability of the solutions) in the pyrrole series, a correlation with infrared measurements was desirable (7, 8). In view of a possible relationship between hydrogen-bonding and basicity, the NH frequencies of the pyrroles were examined.

#### Materials

Substituted pyrroles were synthesized by standard methods (9) or recent variations on these methods (10, 11). Pyrrole was a commercial sample (Fisher) repeatedly redistilled to give a fraction of 1° boiling range; other liquid compounds were distilled similarly. Tetramethyl pyrrole was crystallized from heptane.

The hydrochlorides were prepared as described earlier (5). 2,3,4,5-Tetramethyl pyrrole hydrochloride forms deliquescent white needles of low melting point and regenerates the parent base (melting point and mixed melting point) on treatment of the salt with sodium acetate. The salt slowly decomposes when stored *in vacuo*; the decomposition is not obvious from the condition of the solid but is observed by a slow decrease in the intensity of the ultraviolet absorption.

Infrared spectrum of IIb ( $R_2 = R_3 = R_4 = \text{CH}_3$ ,  $R_5 = \text{H}$ ) (fluorolube mull): 2860, 2810, 2680, 2610 (broad), 1755, 1650, 1574, 1478, 1446, 1412, 1382  $\text{cm}^{-1}$ .

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Infrared spectrum of IIb ( $R_n = \text{CH}_3$ ) (nujol mull); 2680, 2490 (broad), 1780, 1655, 1580, 1415  $\text{cm}^{-1}$ .

$\text{CH}_3\text{OD}$  and  $\text{DCl}$  in  $\text{D}_2\text{O}$  were kindly provided by Dr. L. C. Leitch.

### EXPERIMENTAL

The NMR spectrometer has been described previously (12). The spectra were measured at 60 Mc/s and the chemical shifts are given in c.p.s. from an internal dioxane reference, high field being positive. The internal reference was used in order to remove bulk susceptibility corrections. However, the position of the dioxane reference may change with the change in the acidity of the medium. This change would be expected to be only of the order of a few c.p.s. but must be taken into account in any correlation of the chemical shifts of the parent compound and the hydrochloride.

Most of the ultraviolet measurements were made on a Beckmann DU spectrometer, the remainder being determined on a Cary Model 11M instrument.

Buffer solutions, pH 2.2, 2.8, 3.4, and 4.0 were McIlvaine's citric acid - phosphate standards.

Solutions of the solid hydrochlorides containing 0.8-2.5 mg/25 ml were used.

A Perkin-Elmer model 12C infrared spectrometer equipped with LiF prism was used. Very dilute solutions in carbon tetrachloride were used for the determination of the free NH stretching mode of the pyrroles. The condition of infinite dilution was attained by increasing the dilution until the frequency was unaffected by further dilution. To determine the extent of association, a few drops of the liquids were pressed between rock salt plates and the spectrum of the thin film was taken.

In an attempt to measure the basicity of the different pyrroles, a solution of methanol-*d* was made in each pyrrole and the -OD stretching frequency was examined at 'infinite dilution' to ensure the absence of solute-solute interaction (8).

### RESULTS

#### (i) NMR Spectroscopy

The chemical shifts for the parent compounds are shown in Table I. The spin coupling constants are observed only in two cases. In 3,4-dimethyl pyrrole  $J_{12} = J_{15} = 2.3$  c.p.s.

TABLE I  
The chemical shifts of methyl pyrroles

Compound	N-H	Ring protons		Methyls	
		$\alpha$	$\beta$	$\alpha$	$\beta$
2,4-Dimethyl pyrrole	-220	-166	-138	80	84
3,4-Dimethyl pyrrole		-161			95
2,3,4-Trimethyl pyrrole*	-221	-155		92	96, 100
2,3,5-Trimethyl pyrrole			-127	91, 94	96
2,3,4,5-Tetramethyl pyrrole*				94	104

\*In carbon tetrachloride solution; all the others were pure liquids.

and in 2,3,5-trimethyl pyrrole  $J_{14} = 2.1$  c.p.s. In the other ring proton peaks, this interaction is obscured by the additional interactions of the ring protons with the nitrogen nucleus and the methyl protons. The couplings of the methyls to the ring protons are known to be very small ( $\sim 1$  c.p.s.) and are not observed in these spectra. The chemical shift values serve as reference points for the shifts in the hydrochlorides and the coupling

constants are also useful in assigning the various lines. Note that the  $\alpha$ -methyl groups and the  $\alpha$ -ring protons always come to low field of the corresponding  $\beta$ -positions.

The most probable structures for the pyrrole hydrochlorides are shown in Fig. 1. The structure formed by a loose association of the pyrrole ring with a bare proton is not shown and need not be considered as it does not explain the observed spectra. The structures shown, therefore, are formed by the attachment of the proton to I, the nitrogen atom; IIa and b, the  $\alpha$ -carbon atoms; IIIa and b, the  $\beta$ -carbon atoms. The chemical evidence supports structures I or II (3, 4, 5); however, we include III for completeness.

### 2,3,4,5-Tetramethyl Pyrrole

This is the simplest case to consider. Here all the R groups in Fig. 1 are methyl groups and thus structures IIa and b are equivalent as are also IIIa and b. Thus we need to

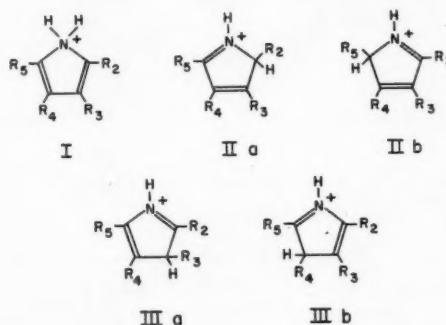


FIG. 1. Possible structures for pyrrole hydrochloride ion.

consider only three possible structures for the hydrochloride. Due to its symmetry the free base has only two methyl resonances, of the  $\alpha$ - and  $\beta$ -methyl groups, at +94 and +104 c.p.s. respectively. If the hydrochloride had structure I this symmetry would be preserved and there would be only two peaks corresponding to the methyl groups, with possibly some fine structure.

The observed spectrum (Fig. 2a) is much too complex to be explained by this structure, which therefore is eliminated. In the observed spectrum, it is difficult to distinguish chemical shift separations from those due to spin interactions. In order to resolve this uncertainty the pyrrole was dissolved in  $\text{DCl}/\text{D}_2\text{O}$ . Any spin interaction with an exchangeable proton (i.e. all protons except those on the methyl groups) will now be reduced by a factor of six. The spectrum of the deuterated pyrrole salt (Fig. 2b) has the same methyl resonances, apart from a spurious peak due to some acetic acid impurity, but the original doublets at +71 and +138 are now broad single lines, proving conclusively the existence of four distinct methyl resonances, two of which are doublets due to spin-spin interaction.

Consider now structures II and III. Both structures would be expected to give rise to four different methyl peaks, one of which (the 2-methyl in II and the 3-methyl in III) will lie to high field, as it is attached to a saturated carbon atom, and give a doublet pattern of separation around 8 c.p.s. due to interaction with the nearest proton. This doublet is seen in the observed spectrum (at +134, +141 c.p.s.) and is strong support for one of these structures. The remaining peaks of the spectrum are less clearly assigned.

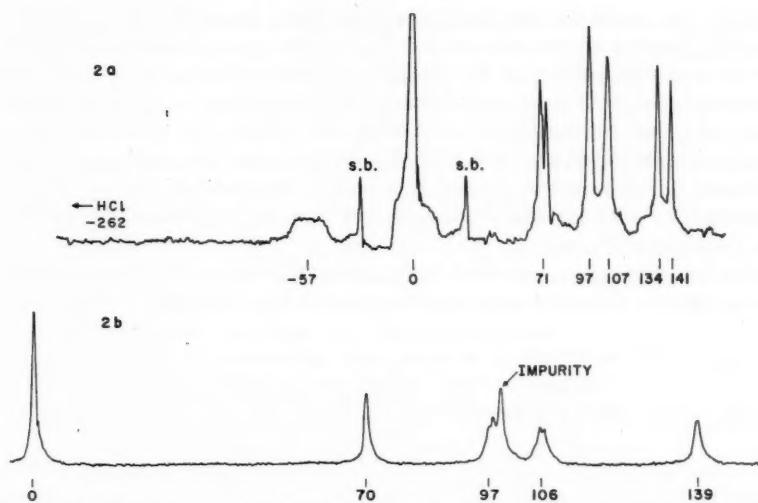


FIG. 2. The NMR spectrum of (a) 2,3,4,5-tetramethyl pyrrole in concentrated HCl, (b) 2,3,4,5-tetramethyl pyrrole in concentrated DCl.

In structure II either of the 3- or 5-methyl peaks could be the low field signal at +71 c.p.s., the 3-methyl as it is now in an  $\alpha$ -position in the ring, and the 5-methyl as it is adjacent to a positively charged nitrogen atom, whilst in structure III it would be expected to be due to the 2-methyl peak. The remaining methyl peaks will be essentially unchanged. Thus from the chemical shift data both structures are possible. However, the doublet fine structure of this signal does provide a further clue. The spin coupling constants in these types of compound are not completely known, but for planar molecules, the methyl ring proton interactions are very small (less than 1 c.p.s. (12)). Thus the 3-c.p.s. splitting of this low field methyl peak is very likely the result of the interaction of the methyl protons with a ring proton which is not in the plane of the ring, i.e. proton 2 or 3, in structure II and III respectively.

However, in structure III, the 3-proton will couple equally with the methyl groups in positions 2 and 4, and thus two of the methyl peaks should be doublets. This is not observed and thus structure III may be discarded.

Thus the ion is very probably structure II. The assignment of the spectrum is then that the low field methyl peak (at +71 c.p.s.) is due to the 3-methyl group, and the remaining methyl peaks at 97 and 107 c.p.s. are assigned to methyls 5 and 4 respectively. The broad hump at -57 is the 2-proton. This has a complex fine structure which would not be expected to be resolved. The N-H proton signal is not observed and the interaction with the nitrogen quadrupole moment would be expected to broaden the peak to such an extent that it would not be observed. The spectrum of the hydrochloride is unchanged on dilution and is given on dissolving the pyrrole hydrochloride in dilute hydrochloric acid. Thus this salt is quite stable in acid solution, in agreement with the chemical evidence.

#### 2,3,4-Trimethyl Pyrrole

The free base has three distinct methyl peaks at 92, 96, and 100 c.p.s. which can be reasonably assigned to the methyl groups in positions 2, 4, and 3 respectively, the 3-methyl being the most shielded. The spectrum of the hydrochloride in concentrated hydrochloric

acid is shown in Fig. 3. The striking feature of this spectrum is the triplet of 2.8-c.p.s. separation given by the low field methyl group.

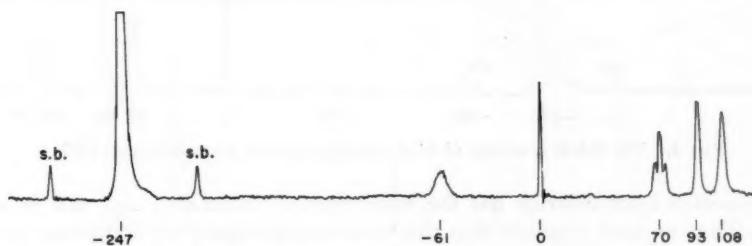


FIG. 3. The NMR spectrum of 2,3,4-trimethyl pyrrole in concentrated HCl.

Consider the possible structures for this ion (Fig. 1). In this case  $R_2$ ,  $R_3$ , and  $R_4$  are methyl groups whilst  $R_5$  is a proton. Structures IIa, IIIa, and IIIb can be eliminated immediately as they would all give the high field doublet observed in the tetramethyl pyrrole hydrochloride. The two remaining possibilities (structures I and IIb) are very similar. Both structures may be expected to give a low field triplet methyl resonance (from the 2-methyl in I and the 4-methyl in IIb), and the other methyl resonances will not differ appreciably from those in the free base; however, the structures can be differentiated by considering the chemical shifts of the ring protons. The resonances of ethylenic protons and protons attached to a positive nitrogen atom are known to lie at very low fields; on the scale used here, at around -150 c.p.s. (Table I) and -260 c.p.s (13) respectively. Thus there are no protons in structure I which would explain the broad peak at -61 c.p.s. However, this can be assigned very simply on structure IIb as due to the  $\text{CH}_2$  protons. The peak is in the correct region (compare the tetramethyl pyrrole hydrochloride in which the corresponding proton is found at -57 c.p.s.), and a further check is provided by the intensity of the peak. The three methyl peaks in Fig. 3 have intensities, in arbitrary units, of 216, 239, and 227 respectively giving an average of  $227 \pm 12$ . The intensity of the low field peak in the same units is equal to 157, which corresponds almost exactly to two-thirds of the intensity of the methyl, i.e. to two protons. The remaining peaks at +93 and +108 c.p.s. can be assigned to the 2- and 3-methyl groups respectively. Their fine structure can arise from coupling between themselves or with the nitrogen hydrogen, in any case it is expected to be small.

Thus the proton magnetic resonance spectrum strongly supports structure IIb in which, as in the case of the tetramethyl pyrrole hydrochloride, the extra proton adds on to an  $\alpha$ -carbon atom in the ring. The spectrum of this salt also does not change appreciably in different solutions, but in very concentrated solutions the individual line widths increase until eventually all the fine structure is obscured. This is probably due to intermolecular interactions rather than to any changes in the structure of the ion.

#### 2,3,5-Trimethyl Pyrrole

The free base has again three distinct methyl peaks at 91, 94, and 96 c.p.s. which can be assigned to the 5-, 2-, and 3-methyl groups, the 3-methyl being the most shielded. The spectrum of the hydrochloride in concentrated hydrochloric acid (Fig. 4) is almost identical with that of the tetramethyl pyrrole hydrochloride with one methyl group missing. This is strong support for the proposed structure of the tetramethyl hydrochloride, as it is the 4-methyl peak in the tetramethyl case which should be missing here

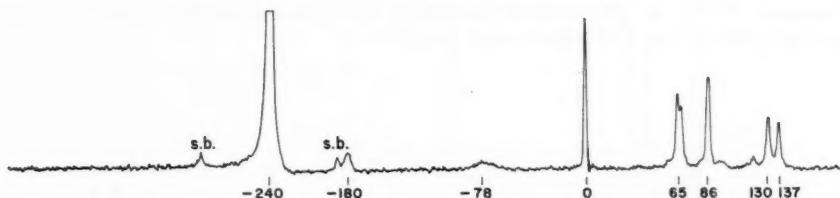


FIG. 4. The NMR spectrum of 2,3,5-trimethyl pyrrole in concentrated HCl.

(if the trimethyl hydrochloride has the same type of structure), and this is what is observed. Thus we may conclude that this structure has again the additional proton on the  $\alpha$ -carbon atom. There are now two possible structures IIa and IIb, i.e. the additional proton is on either the 2- or 5-position. These can be differentiated. The doublet methyl peak at +65 c.p.s. cannot be explained on structure IIb, assuming the values of the ring coupling constants mentioned earlier, but finds a reasonable assignment on structure IIa as the 3-methyl group. The rest of the spectrum is assigned as follows. The 2- and 5-methyl resonances occur at +134 and +86 c.p.s. respectively, the 2-proton is at -78 c.p.s. and the 4-proton at -180 c.p.s.

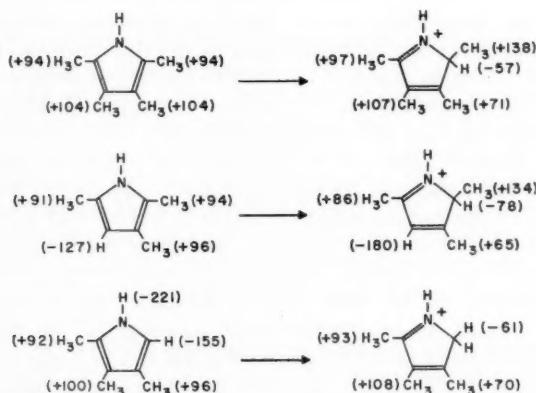


FIG. 5. The chemical shifts and assignments of the protons in the proton magnetic resonance spectra of 2,3,4- and 2,3,5-trimethyl and 2,3,4,5-tetramethyl pyrrole and their hydrochloride ions.

The structures of the remaining pyrrole hydrochlorides studied cannot be determined from their proton magnetic resonance spectra with the same certainty. However, before giving these results, the results for the tri- and tetra-methyl pyrroles are summarized in Fig. 5. Here the chemical shifts and assignments for the free bases and the hydrochlorides are given. The 2,3,4-trimethyl pyrrole formula has been written reversed in the figure so that the similarity with the other structures is more obvious. The figure shows that the differences in chemical shift on going from free bases to hydrochlorides are consistent in these compounds (allowing for the small chemical shift differences in concentration of the solutions and any shift in the internal standard), and these results can now be used to obtain some idea of the structures of the remaining pyrroles studied.

*2,4-Dimethyl Pyrrole*

The spectrum of the hydrochloride in concentrated hydrochloric acid is shown in Fig. 6 (note that the methyl groups are given on a different field scale from the rest of the

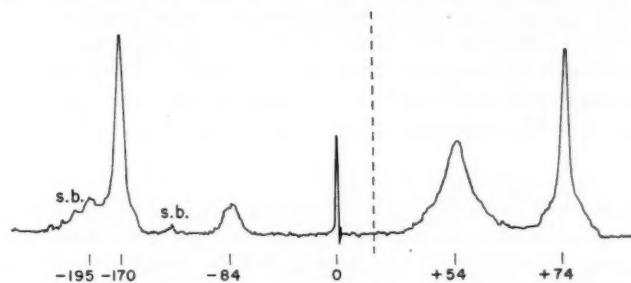


FIG. 6. The NMR spectrum of 2,4-dimethyl pyrrole in concentrated HCl.

spectrum, but that the vertical scale is the same throughout). By exactly similar reasoning to that used in the 2,3,4-trimethyl pyrrole case, it can be shown that the observed spectrum, and in particular the absence of a doublet methyl peak to high field, the breadth of the methyl peak at +54 c.p.s., and the broad peak of intensity two at -84 c.p.s., is explained only by structure IIb, and is inconsistent with any of the other structures. The other dimethyl pyrroles give very different spectra in acid solution. Pyrrole itself is known to trimerize in acid solution (6), and the spectra of the acid solutions of 2,5 and 3,4-dimethyl pyrrole suggest that some reaction has occurred other than the formation of a positive ion. In particular, both compounds give many peaks in the methyl region, 3,4-dimethyl pyrrole gives four broad peaks at +82, 99, 109, and 125 c.p.s. and 2,5-dimethyl pyrrole three main peaks with a considerable amount of fine structure. This suggests that a reaction has occurred with the formation of compounds in which the environment of the methyl groups has changed radically. However, the spectra are difficult to interpret without further chemical evidence.

*(ii)  $pK_a$  Values*

The method reported previously (5) suffers from two disadvantages: (a) The difficulty of ensuring complete solution of the base in the very dilute hydrochloric acid used, and (b) the very limited pH range available, which prevents any check on the values obtained.

The solid salts of the tri- and tetra-substituted pyrroles were dissolved in phosphate-citric acid buffers at pH 2.8, 3.4, and 4.0. The results given in Table II are the average of at least nine determinations per compound (several concentrations). The 'error' quoted represents the spread of values obtained and is not a standard deviation. 2,4-Dimethyl pyrrole was checked by the former method at five different concentrations.

TABLE II  
 $pK_a$ 's of alkyl pyrroles

Pyrrole	$\lambda_{\max}$ (m $\mu$ )	$pK_a$
2,4-Dimethyl pyrrole	249	$1.9 \pm .14$
Cryptopyrrole	260	$3.54 \pm .14$
2,3,4-Trimethyl pyrrole	261	$3.94 \pm .07$
2,3,4,5-Tetramethyl pyrrole	265	$3.77 \pm .16$

It is clear from these values that the incorrect figure reported previously for cryptopyrrole (5) is due to the fact that at the pH used the degree of dissociation being measured was comparable with the error in the method.

(iii) OD Stretching Frequency for Methanol-*d* Dissolved in the Pyrroles

Having established reference  $pK_a$  values by the ultraviolet method, an attempt was made to determine at least the order of the  $pK_a$ 's for other substituted compounds.

The —OD bonding method of Gordy (7) is known to give reasonable agreement within a series of closely related compounds (8). The results recorded in Table III include the

TABLE III  
The OD stretching frequency for methanol-*d* at infinite dilution in pyrroles and  $CCl_4$

Solvent	$\nu_{OD}$ str. ( $cm^{-1}$ )	$\Delta\nu_{OD}$ ( $cm^{-1}$ )
$CCl_4$	2689.5	—
Pyrrole	2522.5*	167
$\alpha$ -Methyl pyrrole	2516	173.5
2,3-Dimethyl pyrrole	2513.5	176
2,4-Dimethyl pyrrole	2516	173.5
2,5-Dimethyl pyrrole	2514.5	175
3,4-Dimethyl pyrrole	2513.5	176
2,3,4-Trimethyl pyrrole	2511.5	178
2,3,5-Trimethyl pyrrole	2514	175.5
Cryptopyrrole	2513	176.5

\*Tamres *et al.* (8) give  $2528\text{ cm}^{-1}$ .

decrease in  $\nu_{OD}$  with respect to the value in  $CCl_4$ . The range of frequency from pyrrole to 2,3,4-trimethyl pyrrole is only  $11\text{ cm}^{-1}$  and since the OD peaks often coincided with solvent peaks and were found by manual plotting, it is not likely that the accuracy obtained ( $\sim \pm 1\text{ cm}^{-1}$ ) permits any conclusion to be drawn about the relative basicities; indeed, the  $\Delta\nu_{OD}$  appears to be quite unrelated to the substitution of the pyrrole.

(iv) Free and Bonded —NH Stretching Frequencies

In view of the inconclusive results above, the extent of association in the substituted pyrroles was determined by measurement of the —NH stretching frequencies in two extreme cases. Table IV gives NH stretching frequencies for the pyrroles at infinite

TABLE IV

Compound	$\nu_{NH}$ str. (infinite dilution in $CCl_4$ )		$\nu_{NH}$ str. (assoc.) pure liquid ( $cm^{-1}$ )	$\Delta\nu$	
	Obs. ( $cm^{-1}$ )	Calc. ( $cm^{-1}$ )		Obs. ( $cm^{-1}$ )	Calc. ( $cm^{-1}$ )
Pyrrole (cf. 15)	3497	3497	3395	102	102
3,4-Dimethyl pyrrole	3501	3501	3393	108	110
2,3-Dimethyl pyrrole	3489	3489	3378	111	111
2,3,4-Trimethyl pyrrole	3490	3491	3375	115	115
2,4-Dimethyl pyrrole	3488	3489	3377	111	111
$\alpha$ -Methyl pyrrole	3486	3487	3379	107	107
Cryptopyrrole	3491	—	3380	111	—
2,5-Dimethyl pyrrole	3477	3477	3365	112	112
2,3,5-Trimethyl pyrrole	3479	3479	3364	115	116
Tetramethyl pyrrole	3480	3481	3360	120	120

dilution in carbon tetrachloride (free molecules) and in the pure liquid (fully associated molecules). The separation  $\Delta\nu_{NH}$  between the free and bonded values is large enough,

according to the Sutherland (28) criterion of  $\Delta\nu/\nu > 3\%$ , to show the existence of hydrogen bonding. The values of  $\Delta\nu_{\text{NH}}$ , which are considered to be a measure of the strength of the hydrogen bond, are included in Table IV.

The NH stretching frequencies of the free molecules and the  $\Delta\nu_{\text{NH}}$  values can be expressed as linear functions of the numbers of  $\alpha$ - and  $\beta$ -substituents. The values are well reproduced by the following formulae

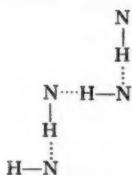
$$[1] \quad \nu_{\text{NH str}} = 3497 - 10n_{\alpha} + 2n_{\beta}$$

$$[2] \quad \Delta\nu_{\text{NH}} = 102 + 5n_{\alpha} + 4n_{\beta}$$

where  $n_{\alpha}$  and  $n_{\beta}$  are the numbers of  $\alpha$ - and  $\beta$ -substituents respectively.

$\Delta\nu_{\text{NH}}$  for 2,5-dimethyl pyrrole is considerably greater than that of pyrrole and the value for 2,3,4,5-tetramethyl pyrrole is the highest of all. Since the strength of the hydrogen bond must increase with  $\Delta\nu_{\text{NH}}$  it seems that steric hindrance by  $\alpha$ -methyl groups has no appreciable inhibitory effect on the strength of the hydrogen bond. This point is emphasized by the fact that the linearity relation (2) is obeyed almost exactly (within the limits of experimental accuracy).

Many suggestions have been made concerning the nature of the association in pyrrole (15-27) and the latest work (27) proposes a zigzag polymer form.



This proposal is also consistent with the results given here for the alkyl pyrroles.

#### DISCUSSION

The ions formed from all four pyrroles which remained as monomers in the aqueous acid are shown to be very probably ions in which the new proton is attached at an  $\alpha$ -carbon in the ring.\*

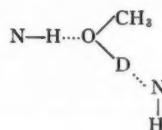
In a series of experiments using pyrroles which were activated by formation of a Grignard derivative, it has been shown (29) that alkylation by an alkyl halide always occurs at an  $\alpha$ -position. In these cases the new alkyl group could be inserted at a substituted  $\alpha$ -position about as easily as at an unsubstituted one when both were available on the same pyrrole. In the protonation reaction, the new proton always adds to the unsubstituted  $\alpha$ -position when the choice exists.

The mull spectra of three hydrochlorides in the crystalline state are so similar in the region 3000-1400  $\text{cm}^{-1}$  as to leave no doubt that the ring structures are identical. The assignments of infrared bands made earlier (5) are still valid, however, and it must be considered possible that the solid phase salts are different in orientation from the salts in solution. In this connection one chemical observation is pertinent. Thus, treatment of 2,3,4,5-tetramethyl pyrrole hydrochloride with water gives an immediate precipitate of the *free base* (melting point) which slowly redissolves in the acid solution. Although this does not prove the hypothesis, it indicates at least that a two-step process involving dissociation and reassociation occurs on dissolution of this salt.

\*Professor G. W. Kenner has kindly informed us that he has also reached this conclusion by similar methods.

This structural assignment gives strong support to the reaction mechanism proposed by Treibs and his co-workers (*inter alios*, 2, 3, 4) by confirming the initial postulate of salt formation.

It was expected that the mechanism of hydrogen bonding in the liquid pyrroles and between methanol-*d* and pyrrole molecules would be very similar, since energetically the processes are presumably almost equivalent. The methanol-*d* solution probably represents the insertion of  $\text{CH}_3\text{OD}$  units into the pyrrole chains, i.e.,



The small range of  $\Delta\nu_{\text{NH}}$  (Table IV) and  $\Delta\nu_{\text{OD}}$  (Table III) agrees with this hypothesis. Thus  $\Delta\nu_{\text{OD}}$  should show the same regular variation with substitution as does  $\Delta\nu_{\text{NH}}$  and it is probably the inaccuracy inherent in the former measurement which prevents this correlation.

It is found that for three pyrroles, the  $\text{p}K_a$  versus  $\Delta\nu_{\text{OD}}$  plot is approximately linear and

[3] 
$$\Delta\nu_{\text{OD}} = 2.3 \text{ p}K_a + 168.$$

Interpolation of other  $\Delta\nu_{\text{OD}}$  values into this equation gives values of  $\text{p}K_a$  which are apparently unrelated to the substitution and do not follow any logical additive principle such as is found for the methyl pyridines (14).

From the known structure of the pyrrole ions, it is reasonable to suggest that a mono- $\alpha$ -substituted pyrrole would form an ion more readily than would a di- $\alpha$ -substituted compound, since the latter involves displacement of a methyl group from the plane of the ring. Thus two distinct series of  $\text{p}K_a$  variations would be expected. This expectation is borne out by the measured  $\text{p}K_a$  values for 2,3,4- and 2,3,4,5-substituted compounds. The  $\Delta\nu_{\text{NH}}$  measurement, which should also reflect basicity, does not show any steric effect of this type and hence does not relate to the basicity measured in solution.

The variations in absorption maximum of the salts with increasing methyl substitution are unusual. Thus (Table II) the addition of the 3-methyl to 2,4-dimethyl pyrrole changes the  $\lambda_{\text{max}}$  by 12 m $\mu$  whilst adding the fourth methyl produces a bathochromic shift of only 4 m $\mu$  (cf. 30). The large increment in  $\text{p}K_a$  accompanying the addition of the third methyl group is also unusual, and the relative positions of substituents, therefore, has a great influence on the salts and also on the ease of salt formation.

The results recorded here add another limit to the value of the hydrogen bonding method for determination of basicity, i.e., that it is necessary to be certain that the hydrogen bond formation is not a radically different process from the salt formation.

#### ACKNOWLEDGMENTS

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## SYNTHESSES IN THE TERPENE SERIES

### VIII. SYNTHESIS OF THE CIS- AND TRANS-ISOMERS OF 7,7,10-TRIMETHYLDECAL-1-ONE. A CONVENIENT MODIFICATION OF THE BROWN HYDRATION REACTION<sup>1,2</sup>

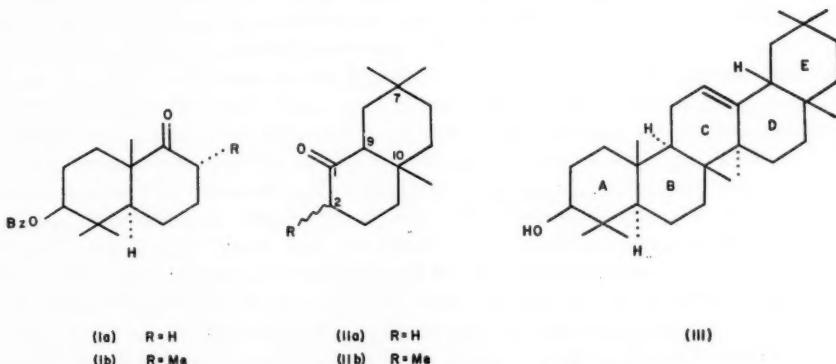
FRANZ SONDHEIMER AND SAUL WOLFE<sup>3</sup>

#### ABSTRACT

7,7,10-Trimethyl- $\Delta^{1(9)}$ -octal-2-one (VII) was converted to the cycloethylenedithioketal (VIII), which on Raney nickel reduction yielded 7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (IX). Oxidation with perbenzoic acid led to the corresponding oxide (X), which could be rearranged in low yield to an equilibrium mixture of 7,7,10-trimethyldecal-1-one consisting essentially of the *trans*-isomer (XI).

A convenient modification of the Brown hydration reaction is described, whereby the necessity of generating diborane or of using diglyme is avoided. 7,7,10-Trimethyl- $\Delta^{1(9)}$ -octalin (IX) on Brown hydration using this modification stereospecifically furnished 7,7,10-trimethyl-*cis*-decal-1 $\beta$ -ol (XII), which was oxidized to 7,7,10-trimethyl-*cis*-decal-1-one (XIII). Isomerization resulted in the above-described equilibrium mixture containing at least 90% of the *trans*-isomer (XI). Similarly, the previously described 10-methyl- $\Delta^{1(9)}$ -octalin (XVI) yielded a mixture of the *cis*- and *trans*-isomers of 10-methyldecal-1-one (XIX). Syntheses of 2-methylene-7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (XIV) and of 7,7,10-trimethyl-*cis*-decal-2,3-dione 3-dithiotrimethylene ketal (XXII) are also described.

In Part V of this series (1) stereospecific syntheses of the bicyclic ketones (Ia) and (Ib) were described, compounds which could become rings A and B of triterpenes of the  $\beta$ -amyrin (III) type. For the construction of rings D and E, ketones of type (II)



are required which are to be joined to the ketones (I) by a two-carbon unit, probably best introduced as acetylene. In this connection a study of the synthesis and stability of 10-methyldecal-1-one has already been carried out (2).

The substances of particular interest are the ketones (IIa) and (IIb) of the *cis*-configuration. Conformational considerations show that the derived acetylenic carbinols on dehydration should give vinyl-acetylenes with the double bond at the required  $\Delta^{1(2)}$ -position, whereas the corresponding *trans*-ketones would be expected to give vinyl-acetylenes with the double bond at the less desirable  $\Delta^{1(6)}$ -position. In this paper we

<sup>1</sup>Manuscript received July 13, 1959.

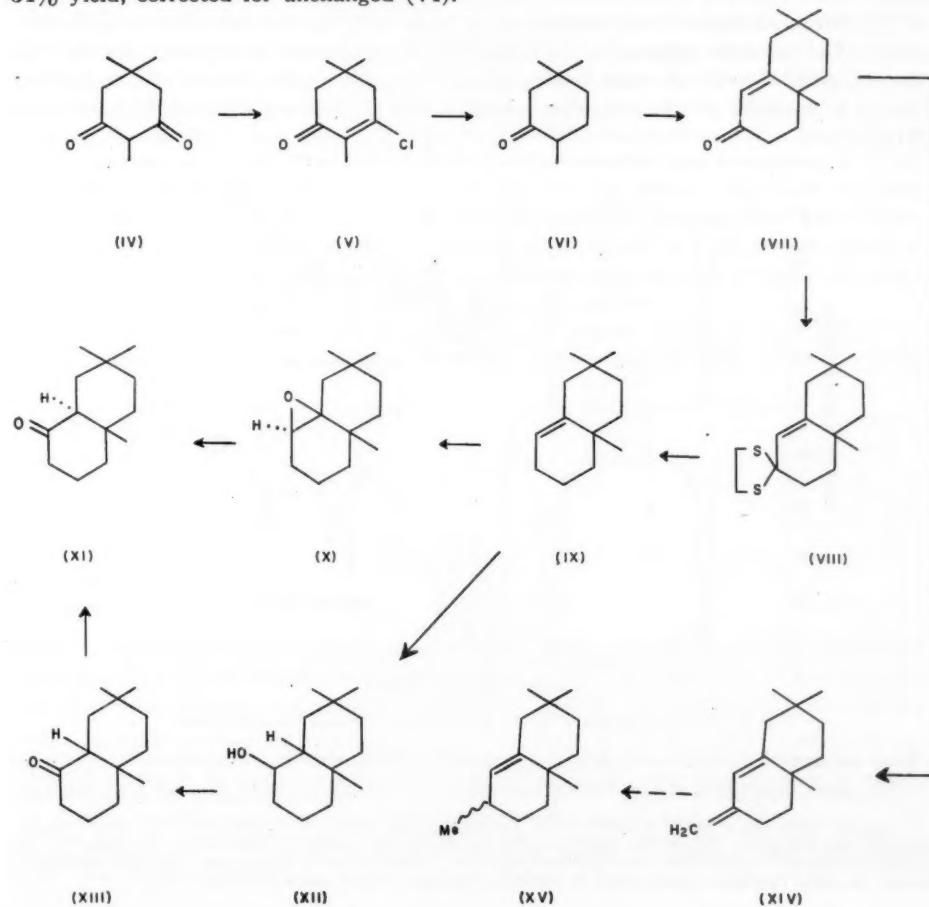
<sup>2</sup>Contribution from the Daniel Sieff Research Institute, The Weizmann Institute of Science, Rehovoth, Israel.

<sup>3</sup>Part VII: Sondheimer, F. and Elad, D. *J. Am. Chem. Soc.* **81**, 4429 (1959).

<sup>3</sup>National Research Council of Canada Postdoctorate Overseas Fellow, 57-1958.

describe a synthesis in good yield of the key intermediate 7,7,10-trimethyl-*cis*-decal-1-one (*cis*-IIa = XIII) as well as its inversion to the corresponding *trans*-isomer (*trans*-IIa = XI).

The starting material for our work was 7,7,10-trimethyl- $\Delta^{1(9)}$ -octal-2-one (VII), obtained by Halsall and Thomas (3) by the route (IV)  $\rightarrow$  (V)  $\rightarrow$  (VI)  $\rightarrow$  (VII). The conversion of 2,5,5-trimethylcyclohexane-1,3-dione (IV) to 2,5,5-trimethylcyclohexanone (VI) has been carried out by two methods (3), the preferred one involving conversion to the enol chloride (V) and subsequent reduction with lithium in ammonia-ethanol and reoxidation. The hydrogenation of the enol chloride (V) over palladium-calcium carbonate in the presence of pyridine (cf. (4)) was reported not to yield (VI). However, in our hands the corresponding reaction when carried out over palladium-charcoal in the absence of pyridine smoothly produced 2,5,5-trimethylcyclohexanone (VI) in 75% yield and this was found to be the best preparative method for obtaining the latter compound. It was found further that the condensation between the ketone (VI) and 4-diethylaminobutan-2-one methiodide could be effected conveniently by the potassium *tert*-butoxide-*tert*-butanol method (2, 5), whereby the octalone (VII) was obtained in 34% yield, corrected for unchanged (VI).



Our first experiments designed to convert the octalone (VII) to 7,7,10-trimethyl-*cis*-decal-1-one (XIII) were modelled after those which led to the successful transformation of 10-methyl- $\Delta^{1(9)}$ -octal-2-one (VII without the 7,7-dimethyl group) to a mixture of the *cis*- and *trans*-isomers of 10-methyldecal-1-one (XIX) (2). Thus, treatment of (VII) with ethanedithiol in the presence of boron trifluoride etherate gave in 91% yield the cycloethylenedithioketal (VIII), m.p. 71°, which on reduction with Raney nickel produced over 80% of 7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (IX). It has been shown that no shift of the double bond occurs in this type of transformation (6).

Oxidation of the octalin (IX) with perbenzoic acid gave a liquid oxide. A model of the olefin (IX) reveals the double bond to be considerably more hindered from the  $\alpha$ - than from the  $\beta$ -side<sup>4</sup> and the oxide is therefore most probably largely, if not completely, the  $\beta$ -oxide (X). The rearrangement of this oxide with boron trifluoride etherate was investigated under a variety of conditions, but in all cases the yield of ketonic material was rather unsatisfactory. Under the optimum conditions (see Experimental) about a 10% yield of a liquid ketone was obtained after chromatography on alumina, Girard separation, conversion to the semicarbazone, and pyruvic acid regeneration. This ketone, the infrared spectrum of which is reproduced in Fig. 1, is an equilibrium mixture of 7,7,10-trimethyldecal-1-one containing at least 90% of the *trans*-isomer (XI) (see below). The material appeared to be reasonably homogeneous, as evidenced by the fact that it yielded directly the pure semicarbazone on being reconverted to this derivative. This is in contrast to the situation which was observed with 10-methyldecal-1-one (XIX) (2).

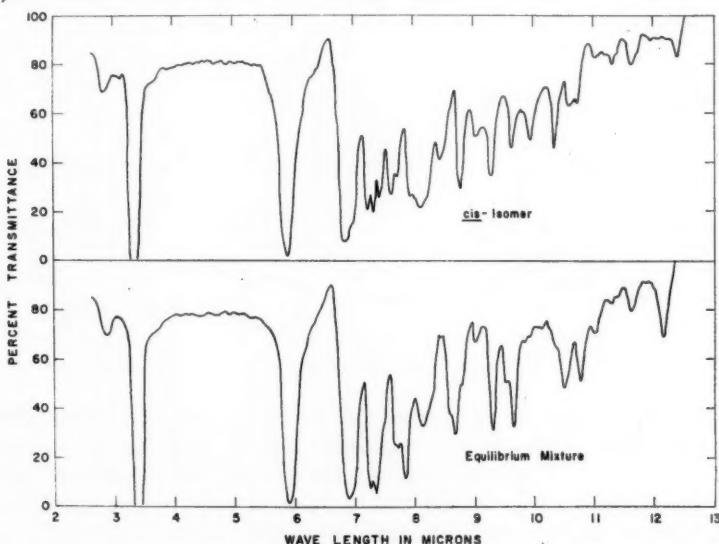


FIG. 1. Infrared spectra of 7,7,10-trimethyldecal-1-ones (in chloroform).

This route to 7,7,10-trimethyldecal-1-one suffers from two disadvantages. Firstly, the yield is poor. Secondly, it has been shown that the rearrangement of oxides to ketones

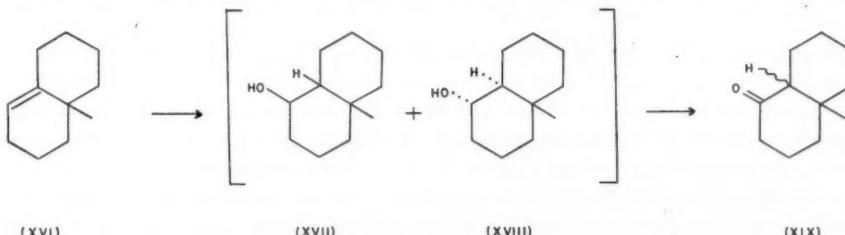
<sup>4</sup>It may be noted that a model of 10-methyl- $\Delta^{1(9)}$ -octalin (XVI) shows the double bond to be about equally hindered from both sides, and, in fact, hydrogenation proceeds about equally from the  $\alpha$ - and the  $\beta$ -side (2). In 7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (IX), the additional equatorial 7 $\beta$ -methyl group appears to make little difference, whereas the axial 7 $\alpha$ -methyl group would be expected effectively to block attack from the  $\alpha$ -side.

proceeds by *cis*-shift of hydrogen (7). The  $\beta$ -oxide (X) will therefore produce the *trans*-decalone (XI) directly, even if care were taken to avoid equilibration of the product during its isolation. This fact, taken together with the apparent stability of the *trans*-ketone (XI), indicates that the more desirable *cis*-isomer (XIII) cannot be obtained by the present method. For these reasons another route to ketones of type (XI) and (XIII) was worked out, as described in the sequel.

An excellent method for the hydration of double bonds has recently been described by H. C. Brown and co-workers. This involves the conversion of the olefin dissolved in an ether to the corresponding trialkylborane by passing in diborane (generated from sodium borohydride and boron trifluoride etherate in diglyme) (8, 9), or alternatively allowing the olefin in diglyme solution to react *in situ* with sodium borohydride and aluminum chloride (10) or with sodium borohydride and boron trifluoride (11). The trialkylborane without purification is then oxidized with alkaline hydrogen peroxide to the borate ester, which under the reaction conditions is hydrolyzed to the corresponding alcohol. The hydration has been shown to proceed by over-all *cis*-addition of water from the less hindered side of the molecule,<sup>5</sup> the hydroxyl function being introduced at the less substituted position (anti-Markownikoff).

Application of the Brown hydration method to  $\Delta^{1(9)}$ -octalins of type (IX) seemed to offer a simple route to ketones of type (XI) and (XIII). However, since no diglyme (diethylene glycol dimethyl ether) was available to us and since the ether-soluble lithium aluminum hydride with boron trifluoride is known also to produce diborane (12), the following modification was made, as exemplified with cyclohexene (for a preliminary communication, see (13)). The latter olefin in ether solution was treated with boron trifluoride etherate and then gradually with an ethereal lithium aluminum hydride solution. The product on oxidation with alkaline hydrogen peroxide then gave cyclohexanol in over 80% yield. Similarly 1-octene was converted to 1-octanol in excellent yield. In this way the necessity of generating diborane separately or of using the high-boiling diglyme (b.p. 160–162° (740 mm)) *in situ* is avoided.

Application of this modification to 10-methyl- $\Delta^{1(9)}$ -octalin (XVI) (2) gave 85% of an alcohol, which judging from our experience in the steroid series (13) and the known



course of hydrogenation of (XVI) (2) is most probably a mixture of 10 $\beta$ -methyl-*cis*-decal-1 $\beta$ -ol (XVII) and 10 $\beta$ -methyl-*trans*-decal-1 $\alpha$ -ol (XVIII). Oxidation of this material with chromium trioxide – pyridine then smoothly yielded 10-methyldecal-1-one (XIX),

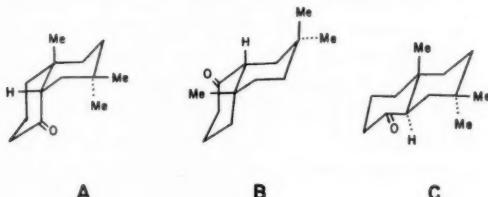
<sup>5</sup>The experiments of Brown, H. C. and Zweifel, G. (J. Am. Chem. Soc. **81**, 247 (1959)) do not provide unequivocal proof that this mode of addition operates in all cases, since they involve flexible monocyclic systems and lead to alcohols in all of which the hydroxyl group is presumably equatorial. Rigid proof for over-all *cis*-addition from the less hindered side (involving *cis*-addition of diborane, followed by oxidation and hydrolysis with retention of configuration) was provided by the demonstration that  $\Delta^5$ -cholestene derivatives on Brown hydration yield the corresponding axial 6 $\beta$ -hydroxycoprostanone as well as the equatorial 6 $\alpha$ -hydroxycholestane derivatives (Wechter, W. J. Chem. & Ind. 294 (1959); Wolfe, S., Nussim, M., Mazur, Y., and Sondheimer, F. J. Org. Chem. **24**, 1054 (1959)).

probably as a mixture of the *cis*- and *trans*-isomers, which gave the same semicarbazone as obtained previously from the equilibrium mixture (2).

Finally our modification of the Brown hydration method was applied to 7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (IX). A crystalline alcohol, m.p. 83°, was readily obtained in 80% yield, which must be 7,7,10 $\beta$ -trimethyl-*cis*-decal-1 $\beta$ -ol (XII) in view of the known steric course of the reaction (9, 13) and the fact that the  $\alpha$ -side of (IX) is considerably more hindered than the  $\beta$ -side.<sup>6</sup> Oxidation of the alcohol (XII) with chromium trioxide-pyridine and direct crystallization of the product then gave 80% of 7,7,10-trimethyl-*cis*-decal-1-one (XIII), m.p. 43°. The infrared spectrum of this ketone, reproduced in Fig. 1, is considerably different from that of the 7,7,10-trimethyldecal-1-one obtained by the first method.

Adsorption of the crystalline *cis*-ketone (XIII) on alkaline alumina resulted in isomerization and yielded the equilibrated product, which was identified with the ketone obtained by the first method in view of the complete identity of the infrared spectra (Fig. 1) and of crystalline derivatives. Comparison of the infrared spectrum of the equilibrated product with that of the crystalline *cis*-ketone (XIII) shows that no more than about 10% of the latter can be present and consequently that it consists essentially of the *trans*-ketone (XI).

Of the two conformations A and B which can be written for the *cis*-ketone (XIII), the latter is undoubtedly the preferred one. It contains three methyl-hydrogen and three methylene-hydrogen 1,3-diaxial interactions, whereas the *trans*-ketone (XI) (conformation C) contains five methyl-hydrogen interactions. The observed greater stability of the latter isomer is therefore in keeping with expectation.



The methylation of the *cis*- and *trans*-isomers of 7,7,10-trimethyldecal-1-one (type IIa) to the corresponding 2,7,7,10-tetramethyl-ketones (type IIb) is now being studied. Some experiments designed to obtain the latter directly have also been carried out and are briefly reported in the sequel, although the desired objective was not reached.

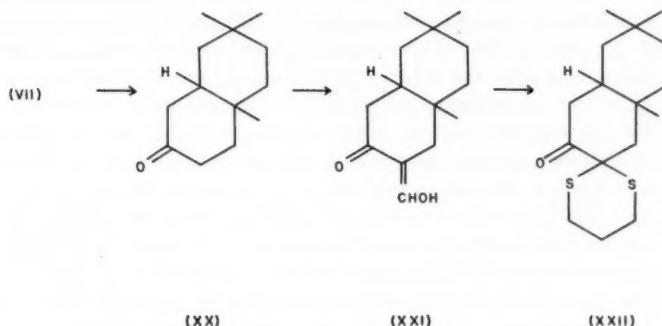
Thus, 7,7,10-trimethyl- $\Delta^{1(9)}$ -octal-2-one (VII) on being subjected to the Wittig reaction (14) with triphenylphosphinomethylene yielded 70% of 2-methylene-7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (XIV). This diene proved to be rather unstable and it was not possible to effect its partial hydrogenation to the corresponding 2-methyl compound (XV), which we intended to hydrate by the Brown reaction.

Hydrogenation of 7,7,10-trimethyl- $\Delta^{1(9)}$ -octal-2-one (VII) with palladium-charcoal in ethanol gave the known 7,7,10-trimethyl-*cis*-decal-2-one (XX), m.p. 68° (3). The 3-position of this compound was blocked through conversion to the 3-hydroxymethylene-ketone (XXI),<sup>7</sup> which with the toluene-*p*-thiosulphonate of propane-1,3-dithiol yielded

<sup>6</sup>See footnote 4.

<sup>7</sup>The formulation of this compound as (XXI) follows from the fact that condensation of *cis*-decal-2-one with ethyl oxalate is known to occur at the 3-position (Stork, G. and Hill, R. K., *J. Am. Chem. Soc.* **79**, 495 (1957)), and in the case of 7,7,10-trimethyl-*cis*-decal-2-one (XX) even normal alkylation and bromination takes place at this position (3).

the dithioketal (XXII), m.p. 121° (method of Woodward *et al.* (15)). This thioketal appears to be a useful substance for further synthetic studies.



### EXPERIMENTAL

Melting points and boiling points are uncorrected. The alumina used for all chromatograms was prepared from Alcoa activated alumina, grade F-20 (Aluminum Co. of America, Pittsburgh, Pa.) through neutralization by means of ethyl acetate and reactivation for 4 hours at 200° (35 mm). Ultraviolet spectra were measured in 95% ethanol solution on a Unicam model S.P. 500 spectrophotometer and infrared spectra in chloroform solution on a Baird double-beam recording spectrophotometer. Analyses were carried out in our microanalytical department under the direction of Mr. Erich Meier.

#### *2,5,5-Trimethyl-3-chlorocyclohex-2-en-1-one* (V)

2,5,5-Trimethylcyclohexane-1,3-dione (IV) was prepared by the methylation of dimedone (3, 16, 17). The reaction of (IV) with phosphorus trichloride was best carried out on a 30–35 g scale under the conditions described by Halsall and Thomas (3). The yield could be improved by azeotropic distillation with dry chloroform of traces of moisture in the ketone (IV) before the addition of the phosphorus trichloride. By taking this precaution, there were obtained from a total of 165 g of IV a total of 125 g (68%) of 2,5,5-trimethyl-3-chlorocyclohex-2-en-1-one, b.p. 78–80° at 2 mm,  $n_{D}^{22}$  1.4963; reported (3): b.p. 76–78° at 5 mm,  $n_{D}^{20}$  1.4962.

#### *2,5,5-Trimethylcyclohexanone* (VI)

A solution of 15 g of 2,5,5-trimethyl-3-chlorocyclohex-2-en-1-one (V) in 165 ml of absolute methanol was shaken with 2 g of a 5% palladium–charcoal catalyst in hydrogen at 22° and 758 mm. The absorption of hydrogen had become very slow after 1 hour, by which time 2.09 molar equivalents of gas had been absorbed. The catalyst was removed and washed well with ethanol. Most of the solvent was removed by fractional distillation through a 12-inch Vigreux column. The residue was dissolved in ether and the solution was washed with water, dried, and evaporated. Distillation of the residue yielded 9.1 g (75%) of 2,5,5-trimethylcyclohexanone, b.p. 79–80° at 21 mm,  $n_{D}^{24}$  1.4458; reported (3): b.p. 71–73° at 12 mm,  $n_{D}^{20}$  1.4460. The semicarbazone showed m.p. 179–180°; reported (3): m.p. 173–177°.

#### *7,7,10-Trimethyl- $\Delta^{1(9)}$ -octal-2-one* (VII)

A solution of potassium *tert*-butoxide in *tert*-butanol (1000 ml of 0.86 N) was added all at once to a boiling solution of 120 g (0.857 mole) of 2,5,5-trimethylcyclohexanone in

200 ml of dry *tert*-butanol under nitrogen. The mixture was boiled for 1 hour under nitrogen and the resulting clear orange solution was allowed to cool to room temperature during the next 2 hours. During this time a solution of 4-diethylaminobutan-2-one methiodide in *tert*-butanol was prepared by the addition of 236 g (1.64 moles) of 4-diethylaminobutan-2-one (18) in 200 ml of dry *tert*-butanol to 230 g (1.62 moles) of methyl iodide in 150 ml of *tert*-butanol, followed by stirring under nitrogen at 0° for 1 hour. The resulting non-viscous two-phase system was added gradually during 1 hour to the solution of the enol, with stirring, whereby the temperature rose to 60° and a reddish suspension resulted. The mixture was stirred in nitrogen at room temperature for 70 hours. It was then poured onto cracked ice containing 180 ml of concentrated hydrochloric acid, and the mixture was well extracted with ether. The organic layer, containing ether and *tert*-butanol, was evaporated, the residue was diluted with ether, and the solution was washed with water, dried, and evaporated. The dark residue was distilled through a small column under reduced pressure. The first fraction after redistillation gave 55 g (46%) of unreacted 2,5,5-trimethylcyclohexanone (b.p. 62–64° at 10 mm; semicarbazone, m.p. 177–179°, undepressed on admixture with an authentic sample). The next fraction (60.5 g) consisted of the crude ketone VII, b.p. 120–125° at 0.7 mm,  $\lambda_{\text{max}}$  241 m $\mu$  ( $\epsilon$  9800). This fraction was converted to the semicarbazone in the usual way. The crude derivative after being filtered and dried weighed 46 g and showed m.p. 208–212°. The derivative could be purified by crystallization, but in practice it was found wasteful and unnecessary to do so. The total crude derivative was therefore boiled under reflux for 30 minutes with 52 g of fused sodium acetate and 40 g of freshly distilled pyruvic acid in 1 l. of glacial acetic acid containing 200 ml of water. Most of the solvent was removed by distillation at 30 mm and ether and water were added to the residue. The ether extract was washed with sodium bicarbonate solution and water, dried, and evaporated. Distillation of the residue yielded 30.2 g (34%, corrected for recovered starting material) of the ketone (VII), b.p. 122–124° at 3 mm,  $n_D^{22}$  1.5068,  $\lambda_{\text{max}}$  241 m $\mu$  ( $\epsilon$ , 16,400); reported (3): b.p. 110–115° (bath) at 0.5 mm,  $n_D^{20}$  1.5070,  $\lambda_{\text{max}}$  243 m $\mu$  ( $\epsilon$ , 17,000). The semicarbazone after crystallization from ethanol showed m.p. 226–227°. Anal. Calc. for  $\text{C}_{14}\text{H}_{23}\text{N}_3\text{O}$ : C, 67.43; H, 9.30. Found: C, 67.22; H, 9.35.

#### 7,7,10-Trimethyl- $\Delta^{1(9)}$ -octal-2-one Cycloethylenedithioketal (VIII)

Boron trifluoride etherate (2 cc) was added to a mixture of 5 g of the unsaturated ketone VII and 4.25 cc of ethanedithiol, with ice-cooling, and the mixture was then allowed to stand at 0° for 30 minutes. The crystalline mass was diluted with 25 cc of dry methanol, cooled, and filtered. This procedure yielded 6.38 g (91%) of the dithioketal (VIII), m.p. 67–69°, which was used in the next step. Crystallization of a small sample from methanol led to the analytical specimen, m.p. 70.5–71°, no high-intensity absorption in the ultraviolet. Anal. Calc. for  $\text{C}_{15}\text{H}_{24}\text{S}_2$ : C, 67.10; H, 9.01. Found: C, 66.86; H, 8.84.

#### 7,7,10-Trimethyl- $\Delta^{1(9)}$ -octalin (IX)

The dithioketal (VIII) (6.3 g), W-2 Raney nickel (ca. 50 g), and absolute ethanol (450 cc) were boiled under reflux for 14 hours. The nickel was removed, washed with absolute ethanol, and the solvent was evaporated through a 12-inch Vigreux column. Pentane was added to the residue, the mixture was filtered, and the filtrate evaporated. Distillation of the residue at 120–130° (bath temperature) at 30 mm yielded 3.40 g (81%) of the olefin (IX),  $n_D^{22}$  1.4951, infrared band at 6.00 and 12.44  $\mu$  (trisubstituted double bond). Anal. Calc. for  $\text{C}_{13}\text{H}_{22}$ : C, 87.56; H, 12.44. Found: C, 87.42; H, 12.20.

The olefin could also be purified by chromatography on alumina and elution with pentane.

*1 $\beta$ ,9 $\beta$ -Oxido-7,7,10-trimethyldecalin (X)*

7,7,10-Trimethyl- $\Delta^{1(9)}$ -octalin (IX) (2 g) (0.0112 mole) in benzene (40 ml) was added during 15 minutes to a solution of perbenzoic acid (0.0123 mole) in benzene (40 ml) cooled to 5°. The solution was then allowed to reach room temperature. Aliquots (0.1 cc each) were removed at intervals and titrated against standard sodium thiosulphate solution. After 15, 30, and 150 minutes the extent of reaction was 88, 95, and 104%, respectively. After the last titration, the solution was washed with 2 N potassium hydroxide solution and water and was then dried and evaporated. Evaporation of the solvent yielded 2.16 g (99%) of the crude oxide (X), which was used for the next step. A small sample was purified by chromatography on alumina, followed by elution with pentane and pentane-benzene (9:1) and finally distillation at 120° (bath temperature) at 23 mm. The purified oxide showed  $n_D^{25}$  1.4868, no infrared band in the 6- $\mu$  region. Anal. Calc. for  $C_{13}H_{22}O$ : C, 80.35; H, 11.41. Found: C, 80.30; H, 11.53.

*Rearrangement of 1 $\beta$ ,9 $\beta$ -Oxido-7,7,10-trimethyldecalin (X) to 7,7,10-Trimethyl-trans-decal-1-one (XI)*

Boron trifluoride etherate (1.78 g) in dry chloroform (25 ml) was added to a solution of the crude oxide (X) (2.0 g) in dry chloroform (25 ml) kept at 0° by ice-cooling. The solution, which rapidly turned orange, was maintained at 0° for 30 minutes and was then poured into 100 ml of a saturated sodium bicarbonate solution. Ether was added and the organic extract was washed with water, dried, and evaporated. The residue (2.02 g) was chromatographed on 80 g of alumina, a procedure which showed it to be a complex mixture. The only ketonic fraction (0.84 g; strong infrared band at 5.84  $\mu$ ) was eluted with pentane-ether (3:1). This fraction did not yield a crystalline semicarbazone. It was therefore boiled under reflux for 1 hour with 2 g of Girard reagent P in 40 cc of absolute methanol containing 4 g of glacial acetic acid. The solution was cooled and added to 5.05 g of sodium bicarbonate dissolved in 250 ml of ice-cold water. The mixture was extracted with ether, and the aqueous layer was then acidified with dilute hydrochloric acid, allowed to stand for 30 minutes, and extracted well with ether. The latter extract was washed with water, dried, and evaporated. The resulting ketone (0.29 g; 14.5%) was converted in about 80% yield into the semicarbazone of the ketone XI, which after crystallization from ethanol showed m.p. 221-222°. Anal. Calc. for  $C_{14}H_{25}N_3O$ : C, 66.89; H, 10.03. Found: C, 66.81; H, 10.21.

The ketone was regenerated from the semicarbazone in over 80% yield with pyruvic acid as described above for the octalone (VII). It showed b.p. 84-86° at 0.1 mm,  $n_D^{25}$  1.4905. The infrared spectrum is reproduced in Fig. 1. Anal. Calc. for  $C_{13}H_{22}O$ : C, 80.35; H, 11.41. Found: C, 80.51; H, 11.43.

Reconversion to the semicarbazone, followed by one crystallization from ethanol, yielded the pure derivative, m.p. 220-222°. The 2,4-dinitrophenylhydrazone after crystallization from ethanol formed orange needles, m.p. 197-198°. Anal. Calc. for  $C_{19}H_{26}N_4O_4$ : C, 60.94; H, 7.00. Found: C, 61.10; H, 6.92.

*Conversion of Cyclohexene to Cyclohexanol with Lithium Aluminum Hydride and Boron Trifluoride*

Boron trifluoride etherate (3.4 g; 0.024 mole) was added to a solution of cyclohexene (4 g; 0.049 mole) in 100 ml of dry ether. A solution of lithium aluminum hydride (0.7 g; 0.018 mole) in 70 ml of ether was then added dropwise during 20 minutes, under

nitrogen, with stirring and ice-cooling. The mixture was stirred at room temperature under nitrogen for a further 2 hours, when 20 ml of acetone were added carefully to destroy excess reagent. A saturated solution of sodium sulphate was added, followed by solid sodium sulphate. The mixture was filtered, the precipitate was washed with ether, and the clear filtrate was evaporated. The residue was dissolved in 30 ml of 90% ethanol containing 0.8 g of sodium hydroxide, and 10.2 ml of 20% aqueous hydrogen peroxide was then added during 5 minutes with stirring, whereby the mixture heated spontaneously to about 70°. The temperature was maintained at this point for 5 minutes longer by external heating and the flask was then cooled. Water and ether were added, the ether extract was washed with water, dried, and evaporated through a Vigreux column. Distillation of the residue yielded 4.0 g (82%) of cyclohexanol, m.p. 20–23°, b.p. 161–162°,  $n_D^{25}$  1.4656, identified with an authentic sample through non-depression of the melting point on admixture and by the complete identity of the infrared spectra.

In exactly the same way, 1-octene was converted in 80% yield to *n*-octanol (b.p. 194–196°,  $n_D^{25}$  1.4295) identified through the infrared spectrum with an authentic sample.

*Conversion of 10-Methyl- $\Delta^{1(9)}$ -octalin (XVI) to *cis*- and *trans*-10-Methyldecal-1-one (XIX) by the Diborane Reaction*

A solution of 0.45 g (0.0032 mole) of boron trifluoride etherate in 5 ml of ether was added to 0.5 g (0.0033 mole) of 10-methyl- $\Delta^{1(9)}$ -octalin (XVI) (2) in 15 ml of ether. A solution of 0.2 g (0.005 mole) of lithium aluminum hydride in 20 ml of ether was then added during 10 minutes under nitrogen with stirring and the mixture was stirred at room temperature for 3 hours more. The product, isolated as before, was dissolved in 15 ml of 90% ethanol containing 0.4 g of sodium hydroxide. The solution was heated to 70° and 1 ml of 20% aqueous hydrogen peroxide was added dropwise. Heating at 70° was continued for 5 minutes and the product was then isolated as above. The resulting material (0.52 g) was chromatographed on 25 g of alumina. Elution with pentane yielded 0.08 g (16%) of unchanged octalin (XVI), while elution with pentane–ether (3:1) gave 0.40 g (71%; 85% corrected for recovered starting material) of a liquid mixture of the carbinols (XVII) and (XVIII), showing a strong hydroxyl band in the infrared.

This material was dissolved in 12 ml of dry pyridine and added dropwise during 10 minutes to a mixture of 0.6 g of chromic acid and 12 ml of pyridine, with stirring and ice-cooling. The mixture was allowed to stand overnight and was then diluted with water and extracted repeatedly with ether. The organic extract was filtered through Celite and evaporated. Distillation of the product at 90–100° (bath temperature) at 3 mm yielded 0.33 g (83%) of a mixture of the *cis*- and *trans*-isomers of 10-methyldecal-1-one (XIX), the infrared spectrum of which was almost identical with that of the previously described equilibrium mixture (2). Conversion to the semicarbazone gave about an 80% yield of derivative, m.p. 198–204°, which after several crystallizations from ethanol rose to 209–210°. The melting point was undepressed on admixture with an authentic sample (m.p. 209–211°) (2).

*7,7,10 $\beta$ -Trimethyl-*cis*-decal-1 $\beta$ -ol (XII) from 7,7,10-Trimethyl- $\Delta^{1(9)}$ -octalin (IX)\**

Boron trifluoride etherate (5 ml) was added to a solution of 2 g of the octalin (IX) in 40 ml of ether. A solution of 1.1 g of lithium aluminum hydride in 70 ml of ether was then added during 45 minutes, with stirring under nitrogen, and the mixture was stirred for another 2 hours at room temperature. The product, isolated as before, was dissolved in 30 ml of 90% ethanol containing 1.2 g of sodium hydroxide. Hydrogen peroxide (7 ml

\*This experiment was done in collaboration with Dr. E. Ghera.

of a 20% solution) was added, and the mixture was allowed to stand at room temperature for 1 hour. Isolation with ether then gave 2.1 g of a product which was chromatographed on 80 g of alumina. Elution with pentane gave 0.12 g (6%) of unchanged octalin (IX), while elution with pentane-ether (4:1) gave 1.65 g (75%; 80% corrected for recovered starting material) of the crystalline alcohol (XII), m.p. 78-81°. Crystallization from pentane gave the analytical sample, m.p. 82-83°, strong hydroxyl band in the infrared. Anal. Calc. for  $C_{13}H_{24}O$ : C, 79.53; H, 12.32. Found: C, 79.87; H, 12.32.

*7,7,10-Trimethyl-cis-decal-1-one (XIII) from 7,7,10-Trimethyl-cis-decal-1β-ol (XII)*

A solution of 2.4 g of the carbinol (XII) in 20 ml of dry pyridine was added during 10 minutes to a mixture of 3 g of chromic acid and 40 ml of pyridine, with stirring and ice-cooling, and the mixture was then allowed to stand at room temperature for 24 hours. The product, isolated as described above, on crystallization from pentane yielded 1.54 g of the *cis*-ketone (XIII), m.p. 40-42°. Distillation of the mother liquors at 120-130° at 25 mm and subsequent crystallization from pentane gave another 0.36 g (total yield, 80%), m.p. 39-42°. Further crystallization from pentane gave large plates, m.p. 42-43°, with the infrared spectrum shown in Fig. 1. Anal. Calc. for  $C_{13}H_{22}O$ : C, 80.35; H, 11.41. Found: C, 80.36; H, 11.23.

*Isomerization of 7,7,10-Trimethyl-cis-decal-1-one (XIII) to the trans-Isomer (XI)*

The crystalline *cis*-ketone (XIII) (0.5 g) dissolved in 10 cc of pentane was absorbed on a column of 50 g of alkaline alumina (Grade F-20, Aluminum Co. of America, Pittsburgh, Pa.), prepared with pentane. The column was then allowed to stand for 12 hours. Elution with pentane and then with pentane-benzene (2:3) yielded 0.47 g (94%) of the liquid equilibrated product, consisting essentially of the *trans*-ketone (XI). The infrared spectrum was identical in every respect with that of the ketone obtained by the boron trifluoride isomerization method. The semicarbazone after crystallization from ethanol formed needles, m.p. 221-222°. The 2,4-dinitrophenylhydrazone formed orange needles from ethanol, m.p. 196-197°. Neither of these melting points were depressed on admixture with the corresponding derivatives of the ketone (XI) obtained from the oxide (X).

*2-Methylene-7,7,10-trimethyl- $\Delta^{1(9)}$ -octalin (XIV)*

An ethereal solution of *n*-butyllithium (35 ml of 0.68 N; 0.024 mole) was added to a suspension of 10 g (0.028 mole) of methyltriphenylphosphonium bromide (prepared from methyl bromide and triphenylphosphine (14)) in 160 ml of dry ether, with swirling under nitrogen. The mixture was stirred in nitrogen for 1½ hours and a solution of 0.96 g (0.005 mole) of the octalone (VII) in 50 ml of ether was added. Stirring at room temperature was continued for 20 hours and 200 ml of dry tetrahydrofuran were then added at the same time as most of the ether was removed by distillation. The resulting mixture was boiled under reflux for 10 hours, cooled, and diluted with water. The product was extracted with ether and the ether layer was washed with dilute hydrochloric acid and water, dried, and evaporated. The orange oily residue was heated with 500 ml of dry pentane, the mixture was cooled, and the triphenylphosphine oxide which had precipitated was removed. Evaporation of the solvent and distillation of the residue gave 0.67 g (71%) of the diene (XIV), b.p. 130-140° (bath temperature), at 23 mm  $n_D^{24}$  1.5100, infrared bands at 6.08 and 11.35  $\mu$ . Anal. Calc. for  $C_{14}H_{22}$ : C, 88.35; H, 11.65. Found: C, 88.60; H, 11.42.

The diene polymerized on attempted chromatographic purification on alkaline alumina and also on being allowed to stand for 1 week in light and air at room temperature.

*7,7,10-Trimethyl-cis-decal-2,3-dione 3-Dithiotrimethylene Ketal (XXII)*

7,7,10-Trimethyl- $\Delta^{1(9)}$ -octal-2-one (1 g) in 200 ml of absolute ethanol was shaken in hydrogen over 0.6 g of a 10% palladium-charcoal catalyst at 755 mm and 25°. After 20 minutes, 1.01 molar equivalents of hydrogen had been absorbed and uptake stopped. The catalyst was removed, the filtrate was evaporated, and the resulting crystalline residue on sublimation at 60° (bath temperature) at 23 mm gave 7,7,10-trimethyl-*cis*-decal-2-one (XX) (0.74 g) as needles, m.p. 65–67°, infrared band at 5.83  $\mu$ ; reported (3): m.p. 67.5–68°.

A solution containing 0.62 g of the *cis*-ketone (XX) and 0.75 ml of freshly distilled ethyl formate in 15 ml of dry benzene was stirred in nitrogen with 0.4 g of sodium hydride at room temperature for 65 hours. Excess hydride was then destroyed by the dropwise addition of methanol, and ether and cold 3% sodium hydroxide solution was added. The aqueous layer was separated, acidified with cold 5% hydrochloric acid, and again extracted with ether. The latter ether extract on being washed with water, dried, and evaporated yielded 1.13 g of the crude hydroxymethylene-ketone (XXI), admixed with formic acid,  $\lambda_{\text{max}}$  282 m $\mu$  ( $\epsilon$ , 5500). This material was dissolved in 25 ml of absolute ethanol, 1.67 g of propane-1,3-dithiol toluene-*p*-thiosulphonate was added, and then a solution of 2.4 g of freshly fused potassium acetate in 10 ml of ethanol. The resulting mixture was boiled under reflux for 5 hours and then evaporated nearly to dryness. Ether and water were added, the organic layer was washed with water, dried, and evaporated. The residue was chromatographed on 30 g of alumina. Elution with benzene yielded 0.42 g (44%) of the dithioketal (XXII) as a crystalline solid, m.p. 100–110°. Two crystallizations from methanol gave the analytical sample as long needles, m.p. 120–121°. Anal. Calc. for  $C_{16}H_{26}OS_2$ : C, 64.38; H, 8.78. Found: C, 64.08; H, 8.59.

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## MYCOCHRYSTONE

### II. CARBON SKELETON, PRINCIPAL CHROMOPHORE, AND OXYGEN FUNCTIONS<sup>1</sup>

G. READ<sup>2</sup> AND L. C. Vining

#### ABSTRACT

A mono- and di-methyl ether and two diacetates of mycochrysone have been prepared. Elemental analyses of these derivatives and of the purified pigment itself are consistent with a revised  $C_{20}H_{12}O_7$  formula for mycochrysone.

The formation of a leucohexaacetate suggests that the molecule contains two hydroxyl or potential hydroxyl oxygen functions in addition to the quinonoid and phenolic (or enolic) groups already shown to be present. The infrared spectra of mycochrysone and derivatives provide evidence that the remaining oxygen atom is ketonic. The principal chromophore of mycochrysone is related to 8-hydroxy-1,2-naphthoquinone. Hydrogenation experiments indicate that the pigment has a perylene carbon skeleton.

#### INTRODUCTION

In part I of this series (1) it was proposed that mycochrysone is a  $C_{20}H_{14}O_7$  peri-hydroxylated orthoquinone containing a second, more acidic, hydroxyl, and since perylene was formed on zinc - zinc chloride fusion, it was concluded that the carbon skeleton was that of either perylene or 1,1'-dinaphthyl.

Several derivatives of the pigment have now been prepared and repeated analyses have given lower hydrogen values than expected for a parent compound of the above formula. Re-examination of the purity of the pigment preparations used in earlier work has now shown that a persistent minor contaminant, not removed by recrystallization from cold chloroform, is responsible for this inconsistency. Recrystallizing the pigment from cold aqueous acetone or by concentrating an ethereal solution at room temperature, or chromatographic purification on silicic acid, has given material analyzing for  $C_{20}H_{12}O_7$ , the molecular formula expected from the analysis of derivatives. The best solvent for purification was cold aqueous acetone. Low and variable carbon analyses had been obtained for the quinoxaline derivative crystallized from methanol (1) and preparations from ethyl acetate give similar results. The derivative is hygroscopic and it appears that complete dessication cannot be obtained.

Methylation of the pigment with silver oxide and methyl iodide at room temperature gave two crystalline compounds, separable by chromatography on silicic acid. The minor product was shown to be a monomethyl ether with properties indicating methylation of the more acidic hydroxyl. The second compound, a dimethyl ether, showed a pronounced hypsochromic shift of the quinonoid absorption band, and tests indicated that in this product the *peri*-hydroxyl group had also been methylated. The monomethyl ether could be readily converted to the dimethyl ether by refluxing with silver oxide in methyl iodide. The incomplete substitution in the cold is not surprising for methylation of *peri*-hydroxyl groups is frequently difficult (2). Both methyl ethers formed quinoxaline derivatives, providing additional evidence for the orthoquinonoid group in mycochrysone. Methylation of mycochrysone quinoxaline at room temperature gave a single

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product shown to be identical with the quinoxaline of the monomethyl ether, a result consistent with the presence of a *peri*-hydroxyl group.

Acetylation by standard techniques failed to yield solid derivatives, and examination of the reactions by paper chromatography indicated that extensive decomposition of the pigment had taken place. The use of silver carbonate with acetic anhydride, however, gave two principal products (mycochrysone acetates I and II) which were separated on a silicic acid - Celite column and found to be isomeric diacetates. Re-examination of the products from acetylation with acetic anhydride and sodium acetate at room temperature by paper chromatography showed that, under these conditions, some mycochrysone acetate I was formed.

Paper chromatographic examination of the crude product from reductive acetylation showed a large number of components. The ultraviolet spectrum of the material indicated that a perylene chromophore was present in low concentration, and in view of the relatively mild reaction conditions this suggested a perylene skeleton in the starting material. The major product, separated by countercurrent distribution, was a hexaacetate. The hydrogen values favored a  $C_{32}H_{28}O_{13}$  formula, but in view of the slightly high carbon analyses and the difficulty experienced with the parent pigment, the compound may be the simple acetylated leucomycochrysone,  $C_{32}H_{26}O_{13}$ . If so the parent compound should contain four hydroxyl groups. The seventh oxygen atom is most probably present in a ketone group since the carbonyl stretching region of the infrared spectra of mycochrysone and all of the derivatives described above contain maxima at or near  $1690\text{ cm}^{-1}$  (s). Should the  $C_{32}H_{28}O_{13}$  formula be correct, it is possible that one or both of the hydroxyl groups not revealed by methylation may have been generated during reduction.

The ultraviolet absorption spectrum of the leucoacetate resembles that of naphthalene, and the principal chromophore of the pigment is therefore similar to that of diosquinone (I),\* isolated from the shrub *Diospyros tricolor* Hiern (Ebenaceae) (3). A comparison between the absorption spectra of these two compounds is shown in Fig. 1. The authors

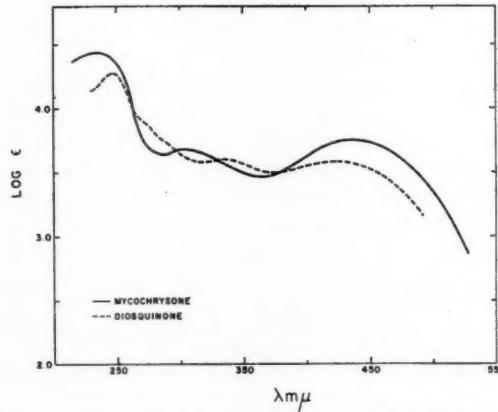


FIG. 1. Absorption spectra in ethanol of mycochrysone and diosquinone (redrawn from (4)).

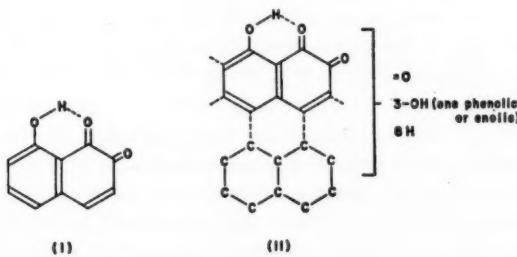
have observed that the ultraviolet spectral properties of a sample of diosquinone changed over a period of several months. Some reservations should therefore be made in accepting

\*This structure has not yet been confirmed by synthesis.

the data obtained by Prista (4), and reproduced here, as an accurate spectrum of this sensitive pigment. Although the two spectra are alike, a closer similarity might have been expected if the naphthaquinone system were the only chromophore present in mycochrysone. In view of the unsaturation in the remainder of the molecule, the differences may be due to an extension of the conjugated system or to an independent chromophore.

The formation of perylene from the pigment by zinc-zinc chloride fusion (1) did not exclude the possibility that mycochrysone is a derivative of 1,1'-dinaphthyl. The identification of the carbon skeleton by a series of reactions less likely to result in cyclized artifacts was therefore sought. It could be expected that hydrogenation followed by dehydration would remove most of the oxygen atoms so that subsequent dehydrogenation of the product might proceed unambiguously to yield the parent hydrocarbon (5). When the pigment was hydrogenated in ethanol or dioxane over Raney nickel, a dark reddish-brown product was obtained and it was evident that decomposition had occurred. However, under similar conditions mycochrysone dimethyl ether reduced smoothly to a colorless oil which yielded a small amount of solid product on trituration with methanol. The solid proved to be tetradecahydroperylene, obtained in 12.5% yield and identified by comparison with an authentic sample. This unexpected result in itself provided convincing evidence for the perylene skeleton, while the production of considerable quantities of perylene from the residual oil on dehydration and dehydrogenation supported the finding. From the dimethyl ether, under somewhat milder conditions, there was obtained a complex mixture of products, some of which appeared to retain the quinol system. Dehydration and dehydrogenation again gave perylene but in lower yields. On no occasion could 1,1'-dinaphthyl be detected.

From a consideration of the results given above, II is suggested as the most probable partial structure for mycochrysone, although the hydroxylic character of two oxygen functions requires confirmation.



## EXPERIMENTAL

Unless otherwise indicated, the petroleum ether referred to in this section has a 60-80° C boiling range.

Whatman No. 1 filter paper disks (32 cm diameter), impregnated with formamide (adjusted with formic acid to pH 6.0), were used for paper chromatograms.

Melting and decomposition points were determined on a Leitz hot stage instrument. Figures given in cases of slow decomposition refer to the first appearance of decomposition. This temperature is largely dependent on the crystal size and is of little diagnostic value.

*Mycochrysone*

The following purifications gave satisfactory products.

(a) Crude mycochrysone, isolated by chloroform extraction (1), was dissolved in acetone and filtered free from a trace of dark impurity. Water was added to the filtrate until it became faintly cloudy and crystals began to form. The solution was refiltered and, on standing overnight at 4° C, gave the bulk of the compound as fine red needles. The crystallization was repeated to give a product slowly decomposing above 195° C. Found: C, 66.00, 66.04%; H, 3.47, 3.37%.  $C_{20}H_{12}O_7$  requires: C, 65.94%; H, 3.32%. Ultraviolet absorption spectrum in ethanol showed  $\lambda_{\text{max}}$  236, 303, 438 m $\mu$ ;  $\log \epsilon$  4.49, 3.75, and 3.80, respectively.

(b) A solution of crude mycochrysone dissolved in "analar" chloroform was filtered and concentrated. The product, which was slowly deposited as orange microcrystals, was redissolved in a large volume of ether. Filtration and concentration of the ethereal solution at room temperature gave mycochrysone as short orange-brown rods, decomposing slowly above 200° C. Found: C, 66.00, 66.27%; H, 3.45, 3.49%.

(c) Crude mycochrysone was adsorbed on a silicic acid column from benzene-chloroform (1:1) and the pigment slowly eluted with chloroform containing 2% ethanol. The product was dissolved in a small volume of acetone and rapidly precipitated with petroleum ether to give mycochrysone as a red amorphous powder decomposing slowly above 175° C. Found: C, 65.92, 65.60%; H, 3.71, 3.69%.

*Mycochrysone Quinoxaline*

The derivative was prepared as in (1); the crude product (100 mg) dissolved in chloroform was applied to a silicic acid column (2.2×6.0 cm). Elution with chloroform-4% ethanol gave the quinoxaline which was crystallized twice from a small volume of ethyl acetate as prisms, slowly decomposing above 228° C.

A sample dried for 16 hours at 140° C and cooled to room temperature under high vacuum was observed to increase steadily in weight while being weighed for analysis. Found: C, 70.68%; H, 3.86%.  $C_{20}H_{16}O_5N_2 \cdot 1/3H_2O$  requires: C, 70.61%; H, 3.80%. A sample (590.08 mg), dried as above, gained 3.26 mg in weight on standing in an open sample tube for 24 hours. Ultraviolet absorption spectrum in ethanol-4% dioxane showed  $\lambda_{\text{max}}$  240, 266.5, 443,  $\lambda_{\text{inf}}$  330 m $\mu$ ;  $\log \epsilon$  4.64, 4.70, 4.17, and 3.95, respectively.

*Methylation (Typical Run)*

Mycochrysone (0.25 g) was shaken for 12 hours at room temperature with silver oxide (0.25 g) and methyl iodide (30 ml) free from hydrogen iodide. The products were washed into chloroform (100 ml Analar), filtered from silver iodide and excess silver oxide, and the filtrate applied to a silicic acid column (4×15 cm). The chloroform eluate gave mycochrysone monomethyl ether (35 mg), deep red needles decomposing slowly above 170° C after three crystallizations from methanol. Found: C, 66.43, 66.74, 66.83%; H, 3.98, 3.86, 3.63%;  $CH_3O$ , 8.79, 9.28%.  $C_{21}H_{14}O_7$  requires: C, 66.67%; H, 3.73%;  $CH_3O$ , 8.21%. Ultraviolet absorption in ethanol showed  $\lambda_{\text{max}}$  235, 301, 443 m $\mu$ ;  $\log \epsilon$  4.50, 3.78, and 3.80, respectively. The monomethyl ether was readily soluble in acetone, dioxane, chloroform, ether, and benzene. In concentrated sulphuric acid, ferric chloride, and sodium hydroxide or sodium carbonate solutions it gave blue, brown, and purple colorations, respectively. It was not extracted from chloroform by sodium bicarbonate solution, and gave a purple solution but no precipitate with methanolic lead acetate.

Development of the column with chloroform containing 3% ethanol eluted mycochrysone dimethyl ether (135 mg), obtained as small, yellow needles, m.p. 251-252° C

(decomp.) after three crystallizations from acetone. Found: C, 67.31, 67.41, 67.47%; H, 4.03, 4.06, 4.16%;  $\text{CH}_3\text{O}$ , 15.08, 15.95%.  $\text{C}_{22}\text{H}_{16}\text{O}_7$  requires: C, 67.34%; H, 4.11%;  $\text{CH}_3\text{O}$ , 15.82%. Ultraviolet absorption in ethanol containing 4% dioxane showed  $\lambda_{\text{max}}$  234, 330, 419  $\text{m}\mu$ ;  $\log \epsilon$  4.58, 3.70, and 3.85, respectively. The dimethyl ether gave a blue solution with concentrated sulphuric acid, dissolved slowly with decomposition in sodium hydroxide, and gave a colorless solution with concentrated ammonia.

Mycochrysone monomethyl ether, mycochrysone dimethyl ether, and mycochrysone had  $R_f$  values of 0.42, 0.20, and 0.07, respectively, when chromatographed on paper by the circular technique using benzene-chloroform (3:1) as mobile phase.

#### *Mycochrysone Monomethyl Ether Quinoxaline*

The quinoxaline of mycochrysone monomethyl ether was prepared in ethanol, purified by elution from a silicic acid column with chloroform, and crystallized from methanol-chloroform (1:1) as needles, m.p. 276-277° C (decomp.). Found: C, 71.69, 71.95%; H, 4.09, 4.07%; N, 6.19%.  $\text{C}_{27}\text{H}_{18}\text{O}_5\text{N}_2$  requires: C, 71.99%; H, 4.03%; N, 6.22%. Ultraviolet absorption in ethanol containing 4% dioxane showed  $\lambda_{\text{max}}$  237.5, 266, 443,  $\lambda_{\text{min}}$  330  $\text{m}\mu$ ;  $\log \epsilon$  4.65, 4.71, 4.11, and 4.00, respectively. The quinoxaline was sparingly soluble in ether, ethyl acetate, benzene, methanol, and ethanol.

Methylation of mycochrysone quinoxaline as above gave a monomethyl ether as needles, m.p. 275-277° C (decomp.). Found: C, 71.75%; H, 4.27%. The ultraviolet and infrared spectra and  $R_f$  of this product were indistinguishable from those of the quinoxaline obtained from mycochrysone monomethyl ether.

#### *Mycochrysone Dimethyl Ether Quinoxaline*

The quinoxaline of mycochrysone dimethyl ether was prepared in glacial acetic acid and purified on a silicic acid column developed with chloroform. The compound was very soluble in common solvents with the exception of ether and petroleum ether and was precipitated from chloroform by petroleum ether as a bright yellow powder, m.p. 175° C. Found: C, 72.26%; H, 4.57%; N, 6.16%.  $\text{C}_{28}\text{H}_{20}\text{O}_5\text{N}_2$  requires: C, 72.40%; H, 4.34%; N, 6.03%. Ultraviolet absorption in ethanol showed  $\lambda_{\text{max}}$  232, 265.5, 423,  $\lambda_{\text{min}}$  324  $\text{m}\mu$ ;  $\log \epsilon$  4.68, 4.73, 4.17, and 4.02, respectively.

The quinoxalines of mycochrysone monomethyl ether, mycochrysone dimethyl ether, and mycochrysone had  $R_f$  values of 0.64, 0.34, and 0.08, respectively, when developed on circular paper chromatograms using petroleum ether-benzene (2:1).

#### *Acetylation with Silver Carbonate and Acetic Anhydride*

Silver carbonate (100 mg) was added to a refluxing solution of mycochrysone (0.5 g) in acetic anhydride (15 ml). After 0.25 hour the solution was cooled, filtered, and poured onto ice. When the acetic anhydride had decomposed, the product (440 mg) was separated by extraction into chloroform and evaporation to dryness under reduced pressure. It showed two main components, acetate I ( $R_f$  0.37) and acetate II ( $R_f$  0.61), when developed on paper chromatograms with petroleum ether-benzene (1:1). The product was dissolved in benzene and adsorbed on a column (38×2.3 cm) of silicic acid-Celite (1:1). Benzene-chloroform (2:1) eluted acetate II which, upon evaporation of the solvent, was left as a brown viscous gum, unstable in hot solvents. Since it could not be crystallized even after further chromatography, it was dissolved in chloroform (5 ml), passed through a fine sintered glass filter, and precipitated by the addition of petroleum ether as a yellow powder (65 mg), m.p. 127-129° C. Found: C, 64.45, 64.50%; H, 3.79, 3.83%; acetyl (Kuhn Roth), 18.52%.  $\text{C}_{24}\text{H}_{16}\text{O}_9$  requires: C, 64.29%; H, 3.60%;  $(\text{OAc})_2$ , 19.2%. Ultraviolet absorption in ethanol showed  $\lambda_{\text{max}}$  244, 296.5, 442  $\text{m}\mu$ ;  $\log \epsilon$  4.37, 3.85, and 3.76, respectively.

Elution of the silicic acid-Celite column with benzene-chloroform (1:1) gave additional acetate II followed by acetate I. After rechromatography on silicic acid the latter product, which was also thermolabile and could not be obtained crystalline, was precipitated as above to give a yellow powder (205 mg), m.p. 142-144° C. Found: C, 64.42, 64.23%; H, 3.74, 3.79%; acetyl (Kuhn Roth), 19.54%. Ultraviolet absorption in ethanol showed  $\lambda_{\text{max}}$  245, 292, 443 m $\mu$ ; log  $\epsilon$  4.39, 3.79, and 3.75, respectively.

#### *Reductive Acetylation*

A solution of mycochrysone (0.4 g) in acetic anhydride (60 ml) was shaken with zinc dust (5 g) for 30 minutes, when it became pale yellow with a bright green fluorescence. Sodium acetate (5 g) was added, the mixture shaken for 30 minutes, and then heated for 40 minutes on a water bath. After cooling and filtration, the solution was poured onto ice and, on decomposition of the acetic anhydride, extracted with chloroform (4  $\times$  50 ml) and the extract evaporated to dryness under reduced pressure. Paper chromatography using petroleum ether-benzene (2:1) showed eight fluorescent bands detected under ultraviolet light in addition to two principal non-fluorescent bands detected by alkaline spray.

Countercurrent fractionation through 200 transfers in the solvent system, water-ethanol-benzene-petroleum ether (2:6:5:3), gave the main component (252 mg) in tubes 66 to 92, with peak concentration in tubes 77 and 78. The material in tubes 76 to 79 (83 mg) was considered pure and was precipitated with petroleum ether (100-120° C) as a colorless powder. It could not be crystallized but melted at 133-135° C. Found: C, 62.14, 62.12%; H, 4.68, 4.63%; acetyl, 43.3, 42.0%.  $\text{C}_{32}\text{H}_{26}\text{O}_{13}$  requires: C, 62.14%; H, 4.24%;  $(\text{OAc})_6$ , 41.7%. Ultraviolet absorption in ethanol showed  $\lambda_{\text{max}}$  227, 292,  $\lambda_{\text{min}}$  326 m $\mu$ ; log  $\epsilon$  4.95, 4.12, and 3.57, respectively.

#### *Hydrogenation of Mycochrysone Dimethyl Ether*

Mycochrysone dimethyl ether (1 g) was hydrogenated in ethanol (60 ml) with Raney nickel for 10 hours at 2000 lb/sq. in. and 200° C. Evaporation of the solvent yielded a colorless viscous oil which on trituration with methanol deposited a solid (85 mg). Crystallization from methanol and sublimation (110° C; 0.05 mm) raised the melting point from 155° to 170° C. Found: C, 89.99%; H, 9.96%.  $\text{C}_{20}\text{H}_{26}$  requires: C, 90.16%; H, 9.84%. Ultraviolet absorption spectrum in heptane showed  $\lambda_{\text{max}}$  274 m $\mu$ ; log  $\epsilon$  3.07. The melting point of this product was undepressed on admixing with an authentic sample of tetradecahydroperylene obtained by hydrogenating perylene (100 mg) under the same conditions. Found: C, 90.35%; H, 9.89%. The ultraviolet and infrared absorption spectra of the two materials were indistinguishable. Literature gives m.p. 175-177° C (6) and  $\lambda_{\text{max}}$  270 m $\mu$ ; log  $\epsilon$  3.38 for the ultraviolet absorption in hexane (7).

The residual oil from the reaction was refluxed for 2 hours with a small amount of cymene over freshly fused and powdered potassium hydrogen sulphate at 180° C. On cooling, the products were freed from inorganic salt by extraction into benzene and chromatographed on an alumina column (45  $\times$  2.3 cm). In addition to cymene, four fractions were collected: (a) 145 mg and (b) 86 mg in the benzene eluate, (c) 74 mg in the chloroform-ethanol (1:1), and (d) 80 mg in the ethanol eluates, respectively. Fractions (a) and (b) gave perylene (78 and 40 mg, respectively) on heating for 3 hours with selenium powder at 290° C, while (c) and (d) yielded small amounts of perylene together with unidentified oils under the same conditions. The perylene was isolated by column chromatography and identified by melting point and ultraviolet absorption (1).

## ACKNOWLEDGMENTS

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## CONDUCTANCES OF DILUTE SOLUTIONS OF POTASSIUM IODATE IN WATER AND WATER-DIOXANE MIXTURES AT 25° C<sup>1</sup>

E. BOCK

### ABSTRACT

Conductances of dilute solutions of potassium iodate in water and water-dioxane solutions, extending over the dielectric constant range from  $D = 78.54$  to  $D = 29.71$ , have been measured over the concentration range from zero up to  $K_A < 0.2$  at 25.00° C. By applying the Fuoss-Onsager treatment to the data obtained, the association constants for the electrolyte in the various solvents, as well as  $\bar{a}$ , the distance of closest approach of the ions, have been determined.

### INTRODUCTION

In the literature are recorded several attempts at calculating association constants of a number of moderately strong electrolytes by means of conductance data. According to the latest refinement of the electrolytic conductance theory by Fuoss and Onsager (1) all these earlier attempts have yielded erroneous association constants, since in their derivation an incomplete equivalent conductance function was used. More specifically, the early association constants were forced to carry transcendental as well as linear terms of the conductance function, terms which have now become calculable. The Fuoss-Onsager conductance equation provides a means of determining all three parameters usually encountered in conductance work, viz. the limiting equivalent conductance  $\Lambda_0$ , the association constant  $K_A$ , and  $\bar{a}$  the distance of closest approach of the ions.

The assumption that salts of the oxyacids belong to the class of moderately strong electrolytes is of long standing. Thus T. Sheldovsky (2) in 1932 interpreted the anomalous course of the phoreogramms of  $\text{AgNO}_3$  and  $\text{KNO}_3$  by assuming ion association. More recently Monk (3), Krieger and Kilpatrick (4), and especially Spiro (5) have addressed themselves to the problem of determining the extent of ion-association of potassium iodate in aqueous solution. However, since, as already pointed out above, in all these efforts the incomplete conductance function was used, it was thought worth while to reinvestigate the potassium iodate problem, and as it was apparent from the papers of the above workers as well as from results of experiments carried out in this laboratory (6) that the association constant of potassium iodate in aqueous solution is of the order of unity, it was necessary to obtain conductance data in solvents of varying dielectric constants. Moreover as rather reliable dielectric constants (7) as well as viscosity and density (8) data for water-dioxane mixtures were available in the literature, it was decided to study the conductance of potassium iodate in these media.

### EXPERIMENTAL

The experimental technique employed has been recorded elsewhere (9), with the exception that instead of preparing dilute solutions by weight dilution these were prepared by direct addition of dry salt in platinum cups, to the solvent, contained in a Sheldovsky-type conductance cell. The salt, dried in a vacuum oven at 80° C for 36 hours, was weighed out on a Mettler M-5 Grammatic micro-balance having a 2- $\mu\text{g}$  sensitivity.

The dioxane of spectro quality was further purified according to the scheme proposed

<sup>1</sup>Manuscript received July 13, 1959.

Contribution from the Department of Chemistry, University of Manitoba, Winnipeg, Manitoba.

by Hess and Frahm (10). After purification the dioxane had a melting point of 11.75° C and a refractive index of  $n_D^{20} = 1.42246$ . In each and every preparation of a water-dioxane mixture only dioxane freshly distilled from sodium was used. The water-dioxane mixtures were prepared by first passing a stream of nitrogen, which was purified by passage through alkaline pyrogallol, sulphuric acid, ascarite, and two tall water saturators (the latter situated in the same bath in which the conductance measurements were carried out), through conductance water, contained in the conductance cell, for several hours until a steady low conductance value was obtained, usually of the order of  $2.5-3 \times 10^{-7}$  mho. Then dioxane freshly distilled from sodium was added to the water by means of a container similar in design to that described by Martel and Kraus (11). The dielectric constants were interpolated from the work of Critchfield, Gibson, and Hall (7), and the viscosities and densities, the former corrected for the latest value of the viscosity of water (12), from the work of Geddes (8).

The conductances were measured on a Jones conductivity bridge, an oscilloscope serving as a detector. The cell constant was determined using the equation for conductances of dilute aqueous solutions of KCl, proposed by Fuoss *et al.* (13).

The temperature was read on a platinum resistance thermometer calibrated by the National Research Council of Canada.

#### RESULTS AND DISCUSSION

The experimental results are summarized in Table I. Figure 1 shows the plots of  $y$  vs.  $x$ ,

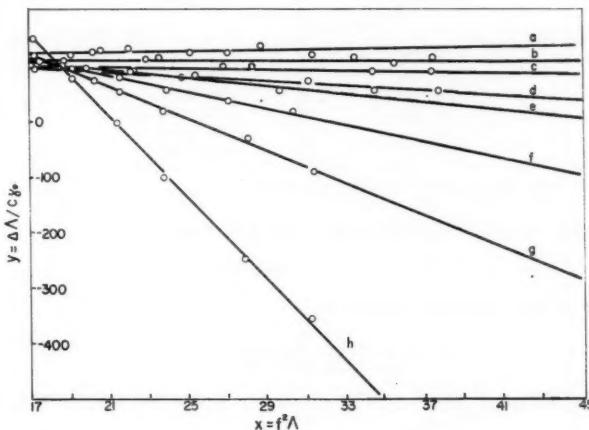


FIG. 1. Plots of  $y$  vs.  $x$ .

Graph: (a) 0% Dioxane. (b) 9.53% Dioxane. (c) 17.94% Dioxane. (d) 29.91% Dioxane. (e) 37.20% Dioxane. (f) 43.79% Dioxane. (g) 49.56% Dioxane. (h) 57.12% Dioxane.

where

$$[1] \quad y = \Delta\Delta/C\gamma_0$$

$$[2] \quad \Delta\Delta = \Delta + Sc^{\frac{1}{2}}\gamma_0^{\frac{1}{2}} - Ec\gamma_0 \log C\gamma_0 - \Delta_0$$

$$[3] \quad x = f^2\Delta.$$

TABLE I  
Equivalent conductances of potassium iodate at various concentrations in different water-dioxane mixtures at 25.00° C

Concentration in moles/l. $\times 10^4$	Equivalent conductance in mhos/equiv.	Concentration in moles/l. $\times 10^4$	Equivalent conductance in mhos/equiv.
0% Dioxane			
0.86082	113.62	1.74644	67.08 <sub>1</sub>
2.05973	113.17	5.17687	66.32 <sub>7</sub>
3.14043	112.90	10.4873	65.56 <sub>5</sub>
4.69655	112.55	28.9172	63.82 <sub>7</sub>
6.58631	112.21	40.4107	63.03 <sub>8</sub>
8.66525	111.87	54.2107	62.24 <sub>2</sub>
10.8189	111.59	71.0788	61.41 <sub>2</sub>
12.9277	111.33		
14.1154	111.19		
15.6428	111.02		
16.8869	111.88		
17.94% Dioxane			
4.13496	82.278	13.3625	94.00 <sub>8</sub>
8.17181	81.63 <sub>2</sub>	25.6002	92.84 <sub>7</sub>
22.8563	80.14 <sub>2</sub>	39.8083	91.88 <sub>4</sub>
41.7615	78.48 <sub>2</sub>	58.6903	90.84 <sub>5</sub>
81.9495	76.87 <sub>6</sub>		
37.20% Dioxane			
17.3233	56.73 <sub>0</sub>	10.6227	46.16 <sub>9</sub>
31.7963	55.48 <sub>8</sub>	21.7473	44.58 <sub>1</sub>
47.2423	54.42 <sub>8</sub>	33.7206	43.32 <sub>6</sub>
61.7318	53.60 <sub>6</sub>	45.2947	42.34 <sub>1</sub>
80.0696	52.71 <sub>6</sub>	53.7218	41.72 <sub>7</sub>
		67.3286	40.85 <sub>4</sub>
		79.2354	40.18 <sub>4</sub>
57.12% Dioxane			
		8.05120	40.694
		14.0987	39.343
		26.3997	37.365
		36.9684	36.127
		50.7410	34.822
		67.0938	33.595

NOTE: These data were taken from a previous publication, see ref. 9.

In Figs. 2 to 6 are shown the graphs of  $\Lambda_1$  vs.  $C\gamma_0$  where

$$[4] \quad \Lambda_1 = \Lambda + Sc^{\frac{1}{2}}\gamma_0^{\frac{1}{2}} - Ec\gamma_0 \log C\gamma_0 + K_A C\gamma_0 f^2 \Lambda$$

and  $\gamma_0$  the degree of association is given by

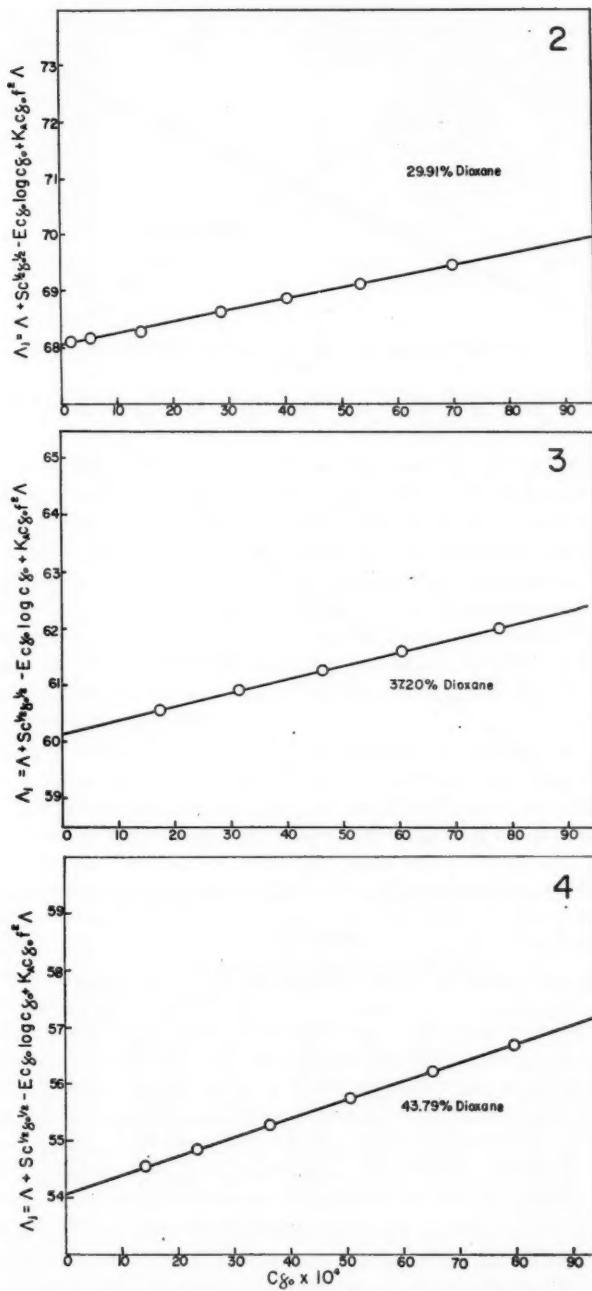
$$[5] \quad \gamma_0 = \frac{\Lambda}{\Lambda_0 - (S(\Lambda c)^{\frac{1}{2}}/\Lambda_0^{\frac{1}{2}})}.$$

Figure 7 shows the plot of  $\log K_A$  vs.  $1/D$ , where  $K_A$  is the association constant for the equilibrium



Lastly Table II summarizes the derived values of  $K_A$ ,  $\Lambda_0$ , and  $d$ ; also included are the values of  $d$  and the corresponding dielectric constants, as well as the weight per cent composition of the solvent, and the Walden product.

As is apparent from Fig. 7,  $\log K_A$  is a linear function of  $1/D$ , a behavior first predicted on theoretical grounds by Denison and Ramsay (14) and later verified experimentally by Kraus *et al.* (15). The linear character of the  $\log K_A$  vs.  $1/D$  plot of course means, as one would expect, that the chief forces involved in ion-pair formation are electrostatic in nature.

FIG. 2. Plot of  $\Lambda_1$  vs.  $c \times 10^3$  (29.91% dioxane).FIG. 3. Plot of  $\Lambda_1$  vs.  $c \times 10^3$  (37.20% dioxane).FIG. 4. Plot of  $\Lambda_1$  vs.  $c \times 10^3$  (43.79% dioxane).

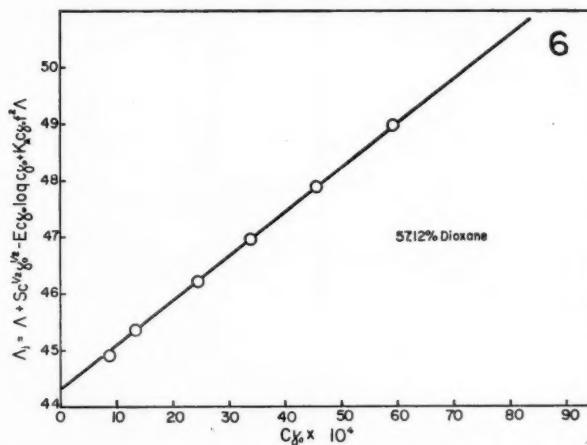
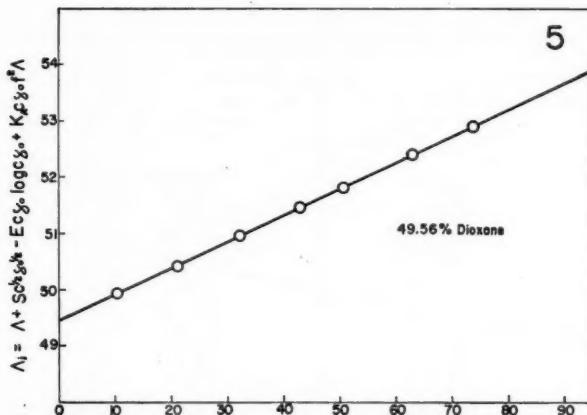
FIG. 5. Plot of  $\Delta_1$  vs.  $c \times 10^2$  (49.56% dioxane).FIG. 6. Plot of  $\Delta_1$  vs.  $c \times 10^2$  (57.12% dioxane).

TABLE II  
Summary of derived quantities

Wt. % dioxane	D	J(d)	d	$K_A$	$\Delta_0$	$\Delta_{070} \times 10^2$
0	78.54	172	(3.2)	.41	114.43	102.27
9.53	70.71	178	(3.2)	.77	96.84	103.85
17.94	63.61	204	(3.2)	1.46	83.84	104.40
29.91	53.27	200	2.8	2.32	68.07	103.09
37.20	41.05	241	2.0	3.92	60.14 <sub>5</sub>	100.75
43.79	41.26	330	3.00	7.85	54.05 <sub>6</sub>	97.91
49.56	36.26	467	3.35	15.1	49.45 <sub>5</sub>	94.53
57.12	29.71	775	3.60	36.8	44.32 <sub>0</sub>	87.94

The graph of  $\log K_A$  vs.  $1/D$  was constructed from the values of  $K_A$  for the five lower dielectric constant media, viz. for mixtures containing 29.91% to 57.12% dioxane. The latter were derived according to the procedure recommended by Fuoss (16) from the slope of the  $y$  vs.  $x$  plot. Only mixtures containing more than 29.91% dioxane yielded a graph of  $y$  vs.  $x$  with a reasonable slope; for a mixture poorer in dioxane than 29.91 the

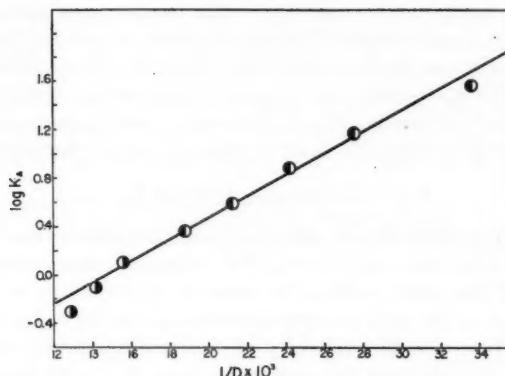


FIG. 7.  $\log K_A$  vs.  $1/D \times 10^3$ . (○) From  $\Lambda_1$  vs.  $c\gamma_0$  plots. (●) From  $y$  vs. plots assuming an  $\delta$  of 3.2 Å.

slope of the  $y$  vs.  $x$  plots were so nearly horizontal that no reliable value of  $K_A$  could be obtained. In these latter cases the  $K_A$ 's were obtained by an alternative procedure, viz. first obtaining the value of  $y(0)$  through extrapolation of the  $y$  vs.  $x$  curve. Then, since at  $x = \Lambda_0 y = y(0) = (J(\delta) - K_A \Lambda_0)$ ,  $K_A$  could be calculated by assuming a value for  $\delta$  and calculating  $J(\delta)$ . The selection of  $\delta$  was in turn guided by the series of  $\delta$  values derived from the slope of the  $\Lambda_1$  vs.  $C\gamma_0$  curve for the five lower dielectric constant mixtures. The limiting equivalent conductances were also derived from these plots. When the logarithms of the association constants thus calculated are plotted vs.  $1/D$  the points fall reasonably close to the straight line of  $\log K_A$  vs.  $1/D$  drawn through the  $\log K_A$  points for the five lower dielectric constant solvents.

From a perusal of Table II it will be noticed that  $\delta$ , the distance of closest approach of the ions, is not constant for the various dielectric constant mixtures, but exhibits a slow increase with decreasing dielectric constant. A similar behavior was noticed by Fuoss and Kraus (17) for  $\text{NaBrO}_3$  (although the increase for this salt was slight it was still noticeable), tetrabutyl ammonium iodide, tetrabutyl ammonium bromide, and tetraisoamyl ammonium nitrate. The change in  $\delta$  in the latter three cases was attributed by the above authors to the disparity of the cationic and anionic sizes. In the case of  $\text{Bu}_4\text{NI}$  it was further suggested that additional induction forces on the periphery of the cation as well as possible specific interactions with the solvent molecules were also causing  $\delta$  to increase in the low dielectric constant region.

Whether similar effects are causing an increase in  $\delta$  in the present case is difficult to say. From an examination of the origin of the  $\delta$  term it would seem that one would expect a change in the magnitude of  $\delta$  with change in the composition of the solvent medium, since  $\delta$  arises out of specifying a boundary condition which demands equality of electrical potential and intensity originating inside and outside a sphere of radius  $\delta$ , on the surface of this sphere. Thus  $\delta$  measures, in a sense, the electrical influence of an ion, an influence which one would expect to change with a change in dielectric constant. The present investigation is of course too incomplete to permit a definite determination of the causes of the increase of  $\delta$  with changing solvent composition, if only because of the fact that all calculations presented in this paper were carried out manually and no second and third approximations in  $\gamma_0$  and  $\Lambda_0$  were attempted. Moreover,  $\Lambda\eta = \Lambda(1 + Fc)$  was approximated to  $\Lambda$  by neglecting the  $Fc$  term for lack of viscosity data but this latter

approximation should not prove too serious in the present case since as suggested by Fuoss (16), for relatively small inorganic ions the  $Fc$  term is unimportant. From the slope of  $\log K_A$  vs.  $1/D$ ,  $d$  results as  $2.8 \text{ \AA}$ ; a value which seems to be unrealistically small. But if as suggested by Fuoss and Kraus, the internal dipole of the iodate ion is taken into account then the steepness of the  $\log K_A$  plot becomes more understandable. Since, if an internal dipole moment is present in one of the ions  $K_A$  should be written as

$$K_A = K_0 \exp (U_1 + U_2)/kT,$$

where  $U_1 = e^2/aD$  is the electrostatic energy of ion-pair dipole in the absence of an internal dipole in one of the ions and  $U_2 = \mu/d^2D$  is the additional energy term resulting from the interaction of the cation with  $\mu$  the internal dipole of the anion. Here  $d$  is the distance from the center of the cation to the electrostatic center of the anion dipole.

There still remains, however, the difficulty of interpreting the equally small  $d$  values derived from the  $y$  vs.  $x$  plots, and the gradual increase of  $d$  with decrease in dielectric constant. Thus the average value of  $d$  derived from  $y$  vs.  $x$  plots results as  $3.2 \text{ \AA}$  which is some  $0.3 \text{ \AA}$  smaller than the sum of the crystallographic radii of the potassium ion ( $1.33 \text{ \AA}$ ), and the iodate ion ( $2.2 \text{ \AA}$ ). This latter value was calculated on the assumption that iodate ion has the shape of a regular tetrahedron of edgelengths  $3.35 \text{ \AA}$  (18).

#### CONCLUSION

In conclusion it may be said that the present paper certainly bears out the predictions of the Fuoss-Onsager conductance equation. There is some difficulty, however, in interpreting the rather small magnitude of  $d$ . If some sort of interpenetration of ionic shells takes place, a possibility which does not seem too inconceivable in the case of the iodate ion considering its tetrahedral or perhaps more correctly, pyramidal structure, then the small value of  $d$  would find an explanation, but this of course is mere conjecture. Further studies of potassium iodate conductances especially in other than water-dioxane mixtures should prove interesting.

Concerning the change of the size of  $d$  with change in dielectric constant of the mixture, attention should be drawn to the fact that the Walden product, almost constant in the region of higher dielectric constants, drops more or less sharply in lower dielectric constant mixtures. Now an increase in  $d$  would of course result in a lowering of the ionic mobility which in turn would result in a decrease of the Walden product. This correlation seems to suggest that the increase of  $d$  in the lower dielectric constant region is perhaps real and does not arise out of some inaccuracies in the experimental data, or the theoretical treatment thereof.

#### ACKNOWLEDGMENTS

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## SENSITIVE VIBRATIONAL FREQUENCIES

### IV. MASS EFFECTS<sup>1</sup>

J. K. WILMSHURST<sup>2</sup>

#### ABSTRACT

The correlation of vibrational frequencies with atomic properties of substituent atoms in the molecular system is critically examined for reality in the light of possible mass effects. The general rule is formulated that only frequencies continuously characteristic of a grouping in the mass-frequency plot can be used in such correlations. Calculated mass-frequency plots are presented for the systems  $XC\equiv N$ ,  $XC\equiv CX$ ,  $XC\equiv CY$ ,  $X_2C=CX_2$ ,  $X_2C=O$ ,  $X_2P=O$ ,  $XCH_3$ ,  $X_2CH_2$ ,  $X_3CH$ .

A number of empirical relations between molecular vibrational frequencies and some property of a substituent atom or radical in the molecular system have recently been reported (1-18), the most common properties used being Hammett's  $\sigma$ -constant (1-7), electronegativity (10-17), and ionization potential (18). However, since all these properties decrease down any column of the periodic table, while any vibrational frequency (for example,  $\nu_{CO}$  in the system  $X_2C=O$ ) will decrease as a substituent (X) in the molecular system is altered down the periodic table, due only to the increasing mass, care must be taken when expressing these empirical relations to ensure that they are indeed real. Ideally, of course, force constants should be evaluated and used (15), but, unfortunately, this is often impracticable for most systems of interest. However, in the absence of force constant data, the characteristic frequency of a bond or group can be used in the empirical correlations provided that firstly its dependence upon the mass of the substituent it is intended to vary is checked. This can be done simply by choosing a potential energy function for the molecular system and plotting the vibrational frequencies as a function of the mass of the substituent which is to be varied. Any significant variation in the slope of the plot of the experimental frequencies from that calculated would then indicate some change in the potential energies of the systems and would hence justify some attempt at a correlation.

In the present investigation calculated plots of frequency versus mass are given for a number of common systems assuming a simple valence force field. These plots show the mass sensitivity of the molecular vibrations and illustrate the phenomenon of "vibrational coupling". Rules are derived to permit rapid qualitative estimates of the mass insensitivity of vibrations and the types of vibrational coupling that may occur in the general case.

#### Secular Determinants

The secular determinants usually encountered in normal co-ordinate calculations are of the form (19):

$$[1] \quad \left| \begin{array}{cccc} A_{11-\lambda}, & A_{12}, & \dots & A_{1n} \\ A_{12}, & A_{22-\lambda}, & \dots & A_{2n} \\ \vdots & \vdots & & \vdots \\ A_{1n}, & A_{2n}, & \dots & A_{nn-\lambda} \end{array} \right| = 0$$

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<sup>2</sup>Contribution from the Department of Chemistry, Auckland University College, Auckland, New Zealand. This work was performed in part at the University of Auckland with financial assistance from the New Zealand University Research Grants Committee.

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where the  $A_{ij}$  are functions of the force constant and masses of a diparticle system (2 atoms for stretching, two bonds for bending, etc.) and  $\lambda = 4\pi^2 c^2 M v^2 (= 5.8894 \times 10^{-2} v^2)$  (19). The  $A_{ij}$  are also functions of the masses and force constants, but are in general smaller than the corresponding  $A_{ii}$  or  $A_{jj}$ .

It is a general property (20) of such symmetrical determinants that the roots of the  $n$ th order determinant are separated by the roots of the diagonal  $(n-1)$ th order determinants which roots are again separated by those of the diagonal  $(n-2)$ th order determinants, and so on. In particular, for the second order determinant:

$$\begin{vmatrix} A_{11-\lambda} & A_{12} \\ A_{12} & A_{22-\lambda} \end{vmatrix} = 0$$

having roots  $\lambda_1, \lambda_2$  ( $\lambda_1 > \lambda_2$ ), then

$$\begin{aligned} [2] \quad \lambda_1 &> A_{11} > \lambda_2 \\ \lambda_1 &> A_{22} > \lambda_2. \end{aligned}$$

Thus, in a symmetry species containing only two vibrational modes, the vibrational frequencies are separated by the frequencies of the two diatom modes. Further, if the frequency-mass plots of the two diatom modes cross (e.g.,  $\sigma$ -frequencies in Fig. 1a), then the pair of frequencies of the system cannot cross, but instead change their vibrational character and in this cross-over region can no longer be defined as approaching a particular diatom mode, but rather are only characteristic of the system as a whole. This is commonly called "vibrational coupling".

If a third order secular equation has roots  $\lambda_1, \lambda_2, \lambda_3$  ( $\lambda_1 > \lambda_2 > \lambda_3$ ) then these are separated by the roots of the three diagonal second order determinants  $\sigma_1, \sigma_2$  ( $\sigma_1 > \sigma_2$ );  $\tau_1, \tau_2$  ( $\tau_1 > \tau_2$ ); and  $\omega_1, \omega_2$  ( $\omega_1 > \omega_2$ ) which are in turn separated by the roots of the first order determinants, giving the following set of inequalities:

$$\begin{aligned} [3] \quad \lambda_1 &> \sigma_1, \tau_1, \omega_1 > \lambda_2 > \sigma_2, \tau_2, \omega_2 > \lambda_3 \\ \sigma_1 &> A_{11}, A_{22} > \sigma_2 \\ \tau_1 &> A_{22}, A_{33} > \tau_2 \\ \omega_1 &> A_{11}, A_{33} > \omega_2. \end{aligned}$$

As with two vibrations in a symmetry species, so in this case with three vibrations it is seen that non-crossing rules apply in the mass-frequency plots. This can be easily extended to higher order determinants and inequality relations similar to eq. [2] and [3] obtained. These inequalities afford a very quick qualitative estimate to be made of the mass-frequency plot and the regions in which vibrational coupling will occur.

Using secular equations derived elsewhere (19, 21, 22, 23, 24) mass-frequency plots have been calculated<sup>8</sup> for a number of simple systems which appear most amenable to empirical correlations, and these are shown in Fig. 1 (XC≡N, XC≡CX, XC≡CY); Fig. 2 (X<sub>2</sub>C=CX<sub>2</sub>, X<sub>2</sub>C=O, X<sub>2</sub>P=O); and Fig. 3 (XCH<sub>3</sub>, CH<sub>2</sub>X<sub>2</sub>, HCX<sub>3</sub>).

#### DISCUSSION

A comparison of the data calculated here with the published empirical correlations shows that in every case the experimental "sensitive" frequency chosen for the empirical correlation varies by a much larger extent than if it were only dependent on mass. Thus,

<sup>8</sup>Though more theoretical significance is attached to the plot of frequency versus  $1/\sqrt{M_X}$ , in order to obtain a better magnification of the curves the frequency was plotted against  $\log M_X$  in the present work. In the symmetry species containing a bending mode the term  $1/r^2_{CX}$  appears and in the calculation of the curves in Figs. 1 and 2a, this has been varied as  $M_X$  varies the standard curve for its variation being obtained by plotting  $r_{CX}$  for the bonds C—H, C—F, C—Cl, C—Br, C—I against the mass of X.

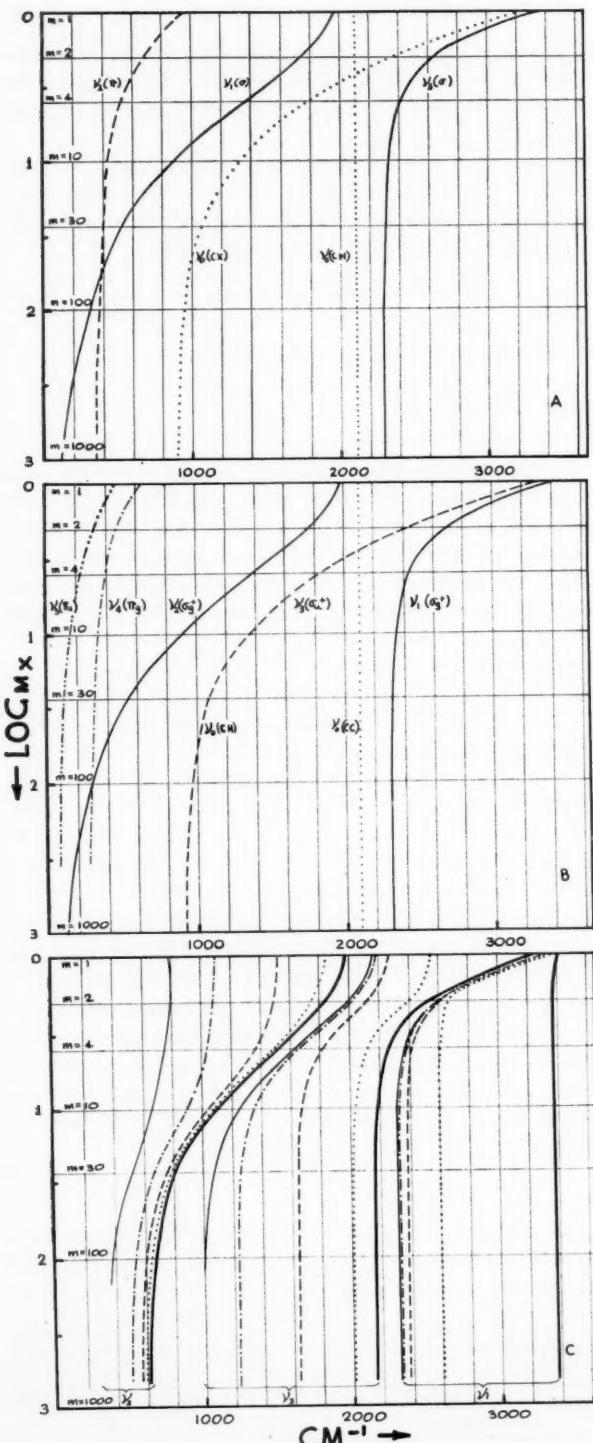
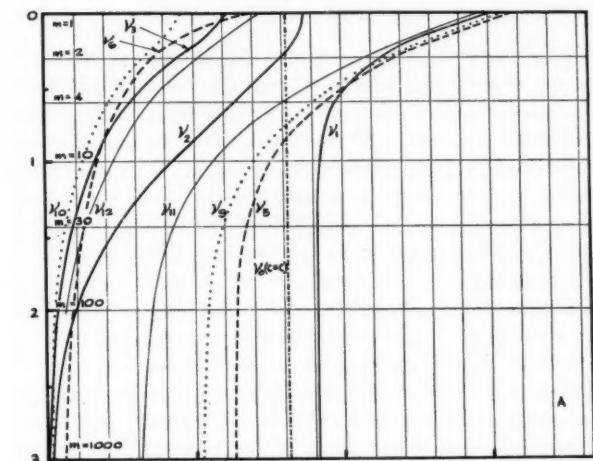
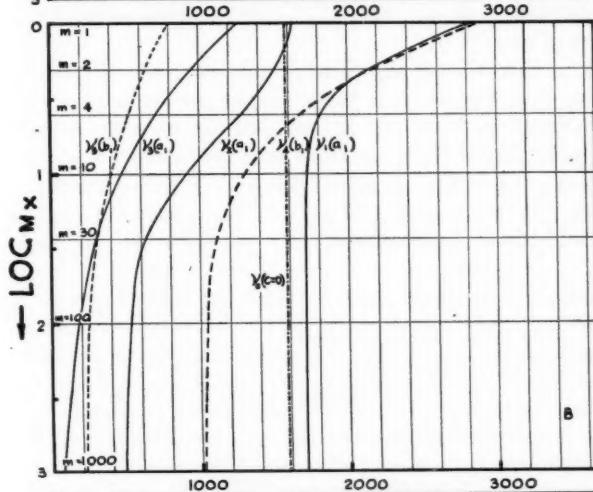


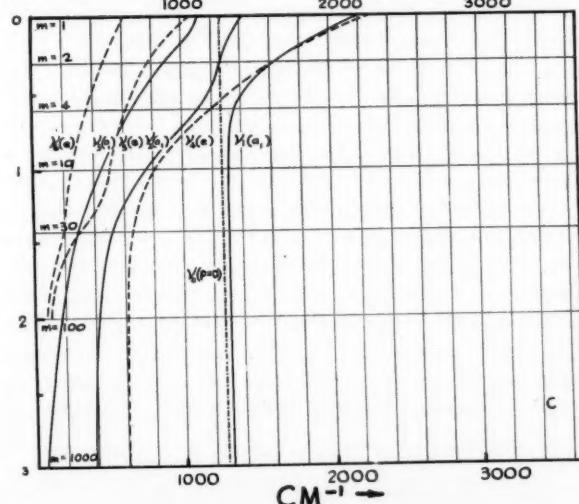
FIG. 1. Calculated mass-frequency curves for:



(a)  $\text{X}_2\text{C}=\text{CX}_2$  ( $k_{\text{CC}} = 9.5 \times 10^5$ ,  $k_{\text{C-X}} = 5.15 \times 10^5$  dynes  $\text{cm}^{-1}$ ,  $\delta_{\text{CCX}} = 0.34 \times 10^{-11}$ ,  $\delta_{\text{XCC}} = 0.57 \times 10^{-11}$  dynes  $\text{cm} \text{ radian}^{-1}$ ) —  $a_s$ ; —  $b_{1s}$ ; . . .  $b_{2u}$ ; - - -  $b_{3u}$ .



(b)  $\text{X}_2\text{C=O}$  ( $k_{\text{C-O}} = 10 \times 10^5$ ,  $k_{\text{C-X}} = 4.45 \times 10^5$ ,  $\delta_{\text{CCX}}/r^2_{\text{CX}} = 0.38 \times 10^6$ ,  $\delta_{\text{XCO}}/r^2_{\text{CX}} = 0.25 \times 10^6$  dynes  $\text{cm}^{-1}$ ).



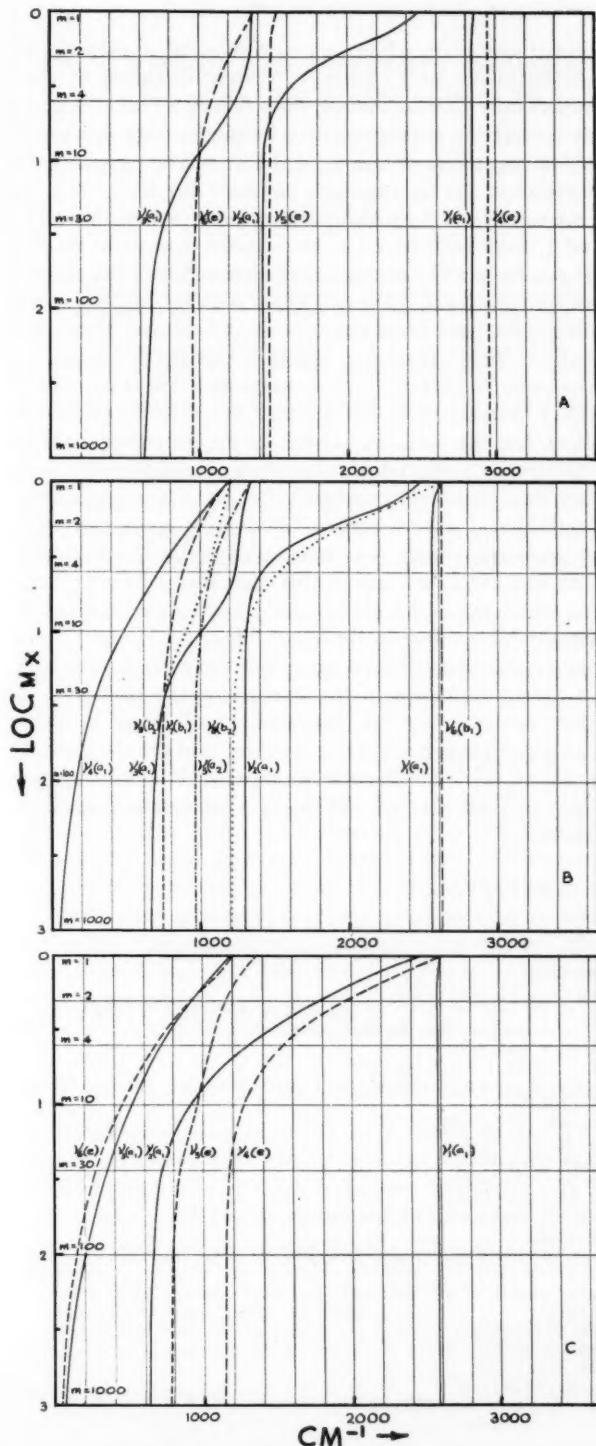
(c)  $\text{X}_3\text{P=O}$  ( $k_{\text{P-O}} = 10 \times 10^5$ ,  $k_{\text{P-X}} = 3 \times 10^5$ ,  $\delta_{\text{XPX}}/r^2_{\text{PX}} = 0.36 \times 10^6$  dynes  $\text{cm}^{-1}$ ).

FIG. 2. Calculated mass-frequency curves for:

in every case it appears the variation of the sensitive frequency with substituent is reflecting a change in potential energy of the system. However, although the variation of vibrational frequency in these systems can then be considered as expressing a variation of potential energy, one fundamental consideration must be remembered before starting any correlations. The region of vibrational coupling in the mass-frequency plot is a cross-over region in which the two interacting frequencies mix, losing their initial characters and emerging with the opposite characters (e.g. Fig. 1a,  $\nu_3$  is a C—X stretching vibration for  $M_X = 1$  and a C≡N stretching vibration for  $M_X > 10$ , while  $\nu_1$  is a C≡N stretching vibration for  $M_X = 1$  and a C—X stretching vibration for  $M_X > 10$ ). If these frequencies are the only two in the symmetry species, or if no interaction with other frequencies in the symmetry species occurs, then they must lie on opposite sides of the corresponding diatom plots (Fig. 1a). In other systems where additional interactions occur, this is modified, but the following general rule still applies. *A frequency characteristic of a particular grouping can only be used in an empirical correlation in that region of the mass-frequency plot where it is continuously characteristic of the vibrational mode.* Thus, in the system XC≡N any correlation of  $\nu_{C≡N}$  with some property of X cannot plot  $\nu_{C≡N}$  for HCN on the same curve as  $\nu_{C≡N}$  for systems with  $M_X > 10$  (Fig. 1a).

This rule has been overlooked in some cases and plots of characteristic frequency versus some atomic property have been constructed using frequencies which are not continuously characteristic of the vibrational mode (10, 11, 12). The apparent agreement of these "improper" points must be considered in these cases as fairly fortuitous, e.g. in the series  $X_2C=O$ ,  $\nu_{C=O}$  for  $H_2C=O$  or for  $HXC=O$  should not be included on the plots of  $\nu_{C=O}$  derived for  $X_2C=O$  and  $XYC=O$  where  $M_X, M_Y > 10$ . The agreement in this case fortuitously arises from the additional interaction of  $\nu_{C=O}$  with  $\delta_{HCH}$  shifting  $\nu_{C=O}$  to higher frequencies.

In other systems such as the benzonitriles where  $\nu_{C≡N}$  is correlated with Hammett's  $\sigma$ -constant of meta- and para-aromatic ring substituents (1, 7) the secular equation virtually factorizes due to the smallness of the interaction (off diagonal) terms between the nitrile group and the ring substituents. In this case the vibrational coupling between  $\nu_{C≡N}$  and the frequencies of the ring substituent will be extremely small and while the non-crossing rule will still apply, both branches of the nitrile curve in the mass-frequency plot will approximate the same straight line for virtually all masses of the substituent and the correlation can be made for all masses of ring substituent. This state of affairs will occur in most cases where the group whose characteristic frequency is being considered is placed a number of atoms away (and is away in space also) from the group whose atomic property is to be correlated. However, since the effect of any group on the characteristic frequency of a vibrating unit decreases rapidly as the group is separated from the vibrating center by atoms in a chain or by space, this approximate factorization is only of interest in conjugated or aromatic systems. In other systems the group affecting the frequency of the vibrating center must be either closely bonded to the center or close in space to it to actually produce any effect on the frequency, and in both cases vibrational coupling will, in general, need to be considered. In the case of orthosubstituted benzonitriles, for instance, the nitrile frequency is not only affected by effects transmitted through the atomic chain, but also because the ortho substituent is close in space to the nitrile group it is affected by the field effect across space. Thus, the approximate factorization will not apply here, as a strong interaction or central force will exist between the nitrile group and the substituent and vibrational coupling will need to be considered in any empirical correlation.



(a)  $\text{CH}_2\text{X}$  ( $k_{\text{C-X}} = 3.6 \times 10^8$ ,  $k_{\text{CH}} = 4.58 \times 10^8$ ,  $\delta_{\text{CH}}/r^2_{\text{CH}} = \delta_{\text{HCH}}/r^2_{\text{CH}} = 0.46 \times 10^8$  dynes  $\text{cm}^{-1}$ ).

(b)  $\text{CH}_2\text{X}_2$  ( $k_{\text{C-X}} = 3.6 \times 10^8$ ,  $k_{\text{CH}} = 3.6 \times 10^8$ ,  $\delta_{\text{CH}}/r^2_{\text{CH}} = \delta_{\text{XCH}}/r^2_{\text{CH}} = \delta_{\text{HCH}}/r^2_{\text{CH}} = 0.36 \times 10^8$  dynes  $\text{cm}^{-1}$ ).

(c)  $\text{HCX}_2$  ( $k_{\text{C-X}} = 3.6 \times 10^8$ ,  $k_{\text{CH}} = 3.6 \times 10^8$ ,  $\delta_{\text{CH}}/r^2_{\text{CH}} = \delta_{\text{XCH}}/r^2_{\text{CH}} = \delta_{\text{HCH}}/r^2_{\text{CH}} = 0.36 \times 10^8$  dynes  $\text{cm}^{-1}$ ).

FIG. 3. Calculated mass-frequency curves for:

In conclusion it should be pointed out that while any variation of a vibrational frequency with changing atomic substituents in a molecular system in excess of that predicted, assuming it were dependent only on mass alone, does reflect a real change in potential energy of the system, any correlation of this sensitive frequency with an atomic property cannot, in general, be verified regardless of how good the correlation appears. In fact, it may quite possibly be fortuitous. As an example, consider the series (13) of methyl derivatives,  $\text{CH}_3\text{X}$ , where the squares of the rocking and symmetrical deformation frequencies for  $\text{X} = \text{F}, \text{Cl}, \text{Br}$ , and  $\text{I}$ , were each found to be linearly dependent on the electronegativity of the halogen. It can be quickly seen on comparison (19) of the experimental data with Fig. 3a that these frequencies in these molecules are varying by a much greater extent than if they were dependent on mass changes alone and are, therefore, reflecting a real variation in potential energy. However, whether this real variation in potential energy is dependent on the electronegativity of  $\text{X}$  as suggested (13) is not established. Fitting other sensitive methyl frequencies to these empirical relations produced estimates of group electronegativities, but the meaning of such group electronegativities is open to the original question of the reality of the relation between potential energy and electronegativity. However, the fact that group electronegativities were later calculated (25) by a completely unrelated method and were found to be in good agreement with those predicted from the empirical frequency versus electronegativity relations does give more credence to the reality of the empirical relations in this case, but it by no means proves them. Although similar uncertainty must be placed on all data obtained from such empirical relations, there is still considerable value in these relations.

As another example, a number of frequency-frequency plots have been obtained (9, 11, 26) and these are often of considerable use to the spectroscopist. However, in setting up these plots care must be taken to obey the non-crossing rule while in using them it must be remembered that an assumption is involved, namely, that the frequencies concerned each depend on the same atomic or molecular properties. This assumption cannot in general be proven and may or may not be valid, a point which should not be forgotten in using these types of relations.

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# CATALYSIS OF THE *CIS-TRANS* ISOMERIZATION OF AZOBENZENE BY ACIDS AND CUPRIC SALTS<sup>1</sup>

STEFANIA CICCONE AND J. HALPERN

## ABSTRACT

The catalytic effects of various acids and metal salts on the *cis-trans* isomerization of azobenzene in aqueous ethanol were examined kinetically. The effect of perchloric acid is apparently due to  $H^+$  ions and is interpreted in terms of a catalytic mechanism involving the conjugate acid of azobenzene. The much greater catalytic effect found for hydrochloric acid is attributed to an additional path involving catalysis by the undissociated acid. Acetic acid was found to be inactive. Of the metal salts examined only those of  $Cu^{++}$  showed pronounced activity which was attributed to co-ordination with the azo group. Kinetic evidence was obtained for a catalytic path involving  $Cu^{++}$  and  $H^+$  simultaneously.

## INTRODUCTION

It has been reported (1, 2) that the *cis-trans* isomerization of azobenzene, which proceeds spontaneously in solution, is susceptible to catalysis by acids, certain metal salts, and a variety of other inorganic and organic substances. However, while the kinetics of the uncatalyzed isomerization have been examined extensively (1, 3), few quantitative measurements have been made on the catalyzed reactions whose mechanisms are thus for the most part unresolved. This paper describes a kinetic study of the catalysis of the isomerization of azobenzene in aqueous alcohol solution by acids and cupric salts and an attempt is made to elucidate the mechanisms of the catalytic effects in these systems.

## EXPERIMENTAL

*Cis*-azobenzene was prepared by the method of Hartley (1) and recrystallized from petroleum ether to a constant melting point of 70°. Distilled water and ethanol, redistilled from KOH, were used as solvents. Cupric perchlorate (G. F. Smith Reagent) was recrystallized from perchloric acid. The acids and other reagents were of reagent grade.

The kinetics of the isomerization reaction were measured using the procedure described earlier (3). The absorption spectra of *cis*- and *trans*-azobenzene were determined in each of the media used and were found to be substantially unaffected by the added acids and metal salts. Solutions of azobenzene were prepared, and all experiments performed, in the dark to prevent photochemical isomerization.

## RESULTS AND DISCUSSION

All the kinetic experiments were made at 60°. The solvent was generally aqueous alcohol in which both azobenzene and the catalysts were conveniently soluble. A few experiments were also made in benzene solution.

Typical rate plots for the uncatalyzed and catalyzed reactions are shown in Fig. 1. The kinetics were generally first order in *cis*-azobenzene yielding a pseudo first order rate constant,  $k$ , which contained contributions from both the uncatalyzed ( $k_0$ ) and catalyzed

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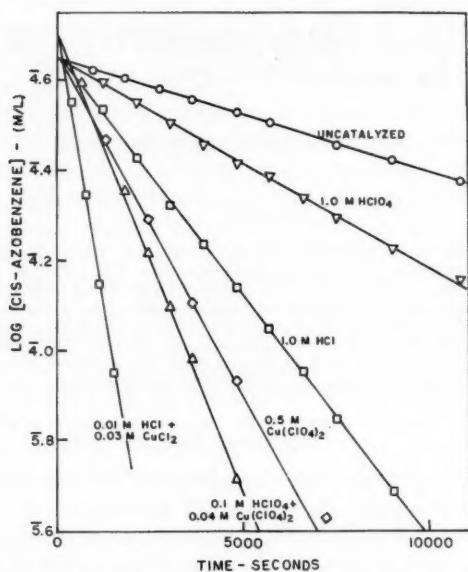


FIG. 1. First order kinetic plots for the uncatalyzed and catalyzed *cis-trans* isomerization of azobenzene in 50 mole % EtOH at 60°.

( $k_{\text{cat}}$ ) paths, i.e.

$$[1] \quad -d[cis\text{-}A]/dt = k[cis\text{-}A]$$

where

$$[2] \quad k = k_0 + k_{\text{cat}},$$

$k_0$  was measured separately and  $k_{\text{cat}}$  determined by difference.

Deviations from first order kinetics were sometimes observed at high catalyst concentrations (particularly with perchloric acid), possibly due to side reactions of azobenzene with the catalyst. In such cases only the region of first order behavior was investigated and the range of results reported below reflects this limitation.

Table I summarizes some of the observed catalytic effects. Of the three acids examined in aqueous alcohol, namely  $\text{HClO}_4$ ,  $\text{HCl}$ , and  $\text{CH}_3\text{COOH}$  (selected as typical strong, intermediate, and weak acids), the first two showed pronounced catalytic activity while the last was inactive. The unimportance of ionic strength effects is indicated by the observation that 0.5 M  $\text{NaClO}_4$  or 0.2 M  $\text{NaCl}$ , either alone or in the presence of equivalent concentrations of the corresponding acid, were substantially without effect.

Since it seemed likely that the acid catalysis was associated with protonation of the azo group, salts of a number of metal ions ( $\text{Cu}^{++}$ ,  $\text{Co}^{++}$ ,  $\text{Ag}^+$ ) with known tendency to coordinate with nitrogen were also examined for catalytic effects. Of these only the cupric salts showed pronounced activity, which was further enhanced in the presence of acids. These effects are discussed further below.

#### Perchloric Acid

The results for this acid, in solvents of various compositions, are summarized in Fig. 2. The range of catalyst concentrations in each case is that for which the kinetics remained first order in *cis*-azobenzene. In this region the catalytic effect conforms to the rate law,

$$[3] \quad k_{\text{cat}} = k_{\text{H}^+} [\text{HClO}_4]$$

TABLE I  
Some catalytic effects at 60°

Solvent	Catalyst	$10^6 k$ (sec <sup>-1</sup> )	$10^6 k_{cat}$ (sec <sup>-1</sup> )
50 mole% EtOH	None	5.8	0.0
50 mole% EtOH	0.1 M HClO <sub>4</sub>	6.4	0.6
50 mole% EtOH	0.5 M HClO <sub>4</sub>	8.6	2.8
50 mole% EtOH	1.0 M HClO <sub>4</sub>	11.2	5.4
50 mole% EtOH	0.5 M NaClO <sub>4</sub>	5.8	0.0
50 mole% EtOH	0.5 M HClO <sub>4</sub> + 0.5 M NaClO <sub>4</sub>	8.6	2.8
50 mole% EtOH	0.2 M HCl	6.4	0.6
50 mole% EtOH	1.0 M HCl	24.2	18.4
50 mole% EtOH	0.2 M NaCl	5.5	-0.3
50 mole% EtOH	0.2 M HCl + 0.2 M NaCl	6.7	0.9
50 mole% EtOH	0.5 M HOAc	5.5	-0.3
50 mole% EtOH	0.5 M KI	5.8	0.0
50 mole% EtOH	0.5 M Cu(ClO <sub>4</sub> ) <sub>2</sub>	35.0	29.2
50 mole% EtOH	0.04 M Cu(ClO <sub>4</sub> ) <sub>2</sub> + 0.1 M HClO <sub>4</sub>	46.0	40.2
50 mole% EtOH	0.03 M CuCl <sub>2</sub> + 0.01 M HCl	101	95
50 mole% EtOH	0.2 M Cu(OAc) <sub>2</sub> + 0.5 M HOAc	15.3	9.5
50 mole% EtOH	0.5 M Co(ClO <sub>4</sub> ) <sub>2</sub> + 0.1 M HClO <sub>4</sub>	6.4	0.6
50 mole% EtOH	0.5 M AgClO <sub>4</sub> + 0.1 M HClO <sub>4</sub>	8.3	2.5
Benzene	None	12.7	0.0
Benzene	0.2 M heptanoic acid	11.2	-1.5
Benzene	0.2 M heptanoic acid + 0.2 M cupric heptanoate	14.3	1.6

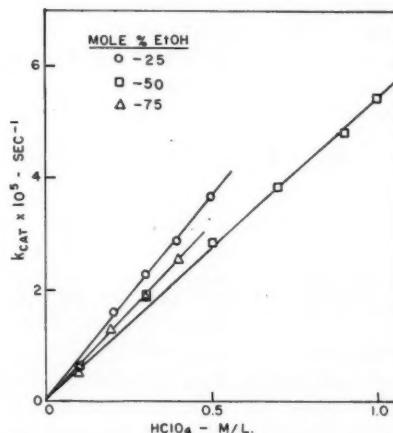
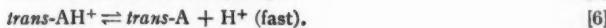


FIG. 2. Catalytic effect of perchloric acid at 60°.

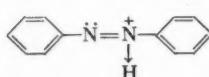
where the values of  $10^6 k_{H^+}$  are 7.4, 5.1, and 6.5 l. mole<sup>-1</sup> sec<sup>-1</sup> in 25, 50, and 75 mole per cent EtOH, respectively.

It seems likely that HClO<sub>4</sub> is completely dissociated in these solutions and hence that the observed catalytic effect is due to H<sup>+</sup> (i.e. H<sub>3</sub>O<sup>+</sup> or EtOH<sub>2</sub><sup>+</sup>) ions. A plausible mechanism, depicted below, assumes that the catalyzed isomerization proceeds through the conjugate acid of azobenzene (AH<sup>+</sup>), formed in a rapid pre-equilibrium step, i.e.

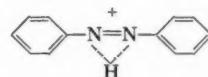


The protonation equilibrium of azobenzene in acidic solutions is well known (4, 5) although, because of the rapid isomerization, it can be studied only for the *trans* isomer. Spectrophotometric measurements have yielded values of  $-2.5$  (4) and  $-1.6$  (5) for  $pK_a$  of  $AH^+$  at  $25^\circ$ . The equilibrium concentration of  $AH^+$  in our solutions is thus very small ( $\sim 1\%$  at  $1\text{ M H}^+$ ) and is not detected spectrophotometrically.

The structure of  $AH^+$  has not been conclusively established. Klotz (4) has proposed structure (I) in which the proton is localized on one of the N atoms through a bond involving lone pair electrons. On the other hand Jaffé (5, 6), on the basis of convincing evidence, favors the non-classical structure (II) in which H is attached to both N atoms through



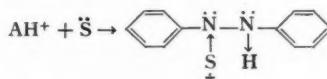
(I)



(II)

delocalized bonds. Enhanced ease of isomerization is more readily explained in terms of the first model where some reduction in the degree of double bond character of the azo bond might be expected through polarization. It is less obvious why structure (II) should lead to enhanced isomerization particularly if, as suggested by Jaffé (5, 6), the *cis*-conformation of this structure is the more stable one.

An alternative description of the slow isomerization step, which we are inclined to favor, involves the attack of a solvent molecule (S) on  $AH^+$  to give an intermediate (III) in which free rotation about the N—N bond is possible, i.e.



[7]

(III)

This mechanism is readily consistent with either structure (I) or (II) for  $AH^+$ .

Zucker and Hammett (7, 8) have suggested a criterion for distinguishing between a mechanism of the type represented by equations [4], [5], and [6] and one in which the rate-determining step [5] is replaced by step [7] involving attack on the conjugate acid by a solvent molecule. This is based on the expectation of a linear dependence of  $k_{cat}$  on  $h_0$  (related to the Hammett acidity function  $H_0$  (9, 10) by  $H_0 = -\log h_0$ ) in the first case and on  $[H^+]$  in the second. Unfortunately this criterion is not readily applicable here in view of the limited acidity range accessible to kinetic measurement and of the absence of  $h_0$  data for mixed solvents. In aqueous solution the dependence of  $h_0$  on  $[H^+]$  does diverge appreciably from linearity even below  $1\text{ M HClO}_4$  and this divergence is not reflected in plots in Fig. 2. On the other hand the dependence of  $k_{cat}$  on solvent composition appears to follow  $h_0$  which, at least for HCl, has been shown to pass through a minimum in the vicinity of equimolar concentrations of  $H_2O$  and  $EtOH$  (11). Because of their conflicting nature, and because of the questionable theoretical validity of the Zucker-Hammett hypothesis (8), these indications are considered as inconclusive. An alternative kinetic interpretation, namely that the protonation step [4] is rate determining, also leads to an expected  $h_0$ , rather than  $[H^+]$ , dependence but is considered unlikely in view of the low rates.

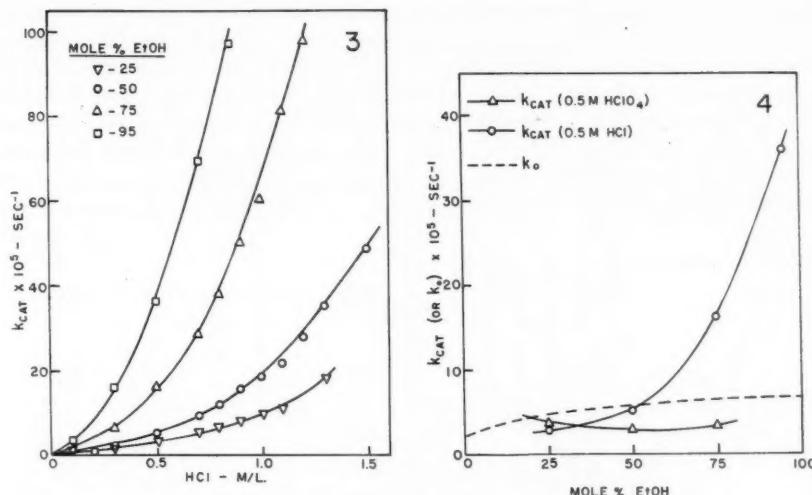


FIG. 3. Catalytic effect of hydrochloric acid at 60°.

FIG. 4. Solvent dependence of the catalytic effects of perchloric and hydrochloric acids at 60°. The broken line depicts the solvent dependence of the uncatalyzed rate ( $k_0$ ).

### Hydrochloric Acid

The results for this acid are depicted in Figs. 3 and 4. Attention is directed to the following features.

- (1) Except at very low concentrations, the catalytic activity of HCl is greater than that of  $\text{HClO}_4$ .
- (2) the kinetic dependence of  $k_{\text{cat}}$  on the total HCl concentration,  $[\text{HCl}]_0$ , is apparently greater than first order.
- (3) The catalytic effect increases markedly with the EtOH content of the medium. At low EtOH content it approaches that of  $\text{HClO}_4$ .

This behavior can be interpreted in terms of a catalytic contribution due to undissociated HCl in addition to that due to  $\text{H}^+$ . The predicted rate law is then

$$[8] \quad k_{\text{cat}} = k_{\text{H}^+} [\text{H}^+] + k_{\text{HCl}} [\text{HCl}]$$

$$[9] \quad = k_{\text{H}^+} [\text{H}^+] + (k_{\text{HCl}}/K) [\text{H}^+] [\text{Cl}^-],$$

where  $K$  is the dissociation constant of HCl. If the fraction of undissociated HCl is small,  $[\text{H}^+] \sim [\text{Cl}^-] \sim [\text{HCl}]_0$ , and equation [9] becomes

$$[10] \quad k_{\text{cat}} = k_{\text{H}^+} [\text{HCl}]_0 + (k_{\text{HCl}}/K) [\text{HCl}]_0^2$$

or

$$[11] \quad k_{\text{cat}}/[\text{HCl}]_0 = k_{\text{H}^+} + (k_{\text{HCl}}/K) [\text{HCl}]_0.$$

The linear plots of  $k_{\text{cat}}/[\text{HCl}]_0$  vs.  $[\text{HCl}]_0$  in Fig. 5 are, on the whole, in accord with this, although their intercepts yield values of  $k_{\text{H}^+}$  which are somewhat lower than those obtained with  $\text{HClO}_4$  (like the latter, however, these pass through a minimum at 50 mole per cent EtOH). Again this may be due to the fact that the  $\text{H}^+$ -catalyzed reaction follows  $k_0$  rather than  $[\text{H}^+]$  and that in these media the former is appreciably lower for HCl than for  $\text{HClO}_4$  even at low concentrations.

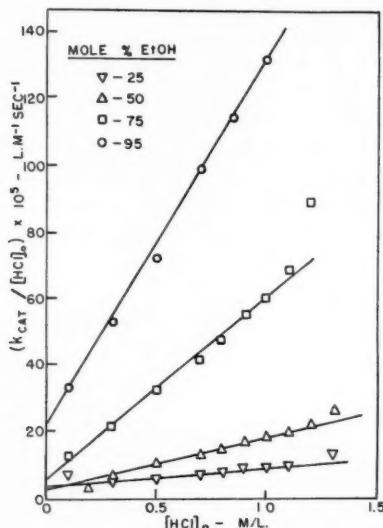
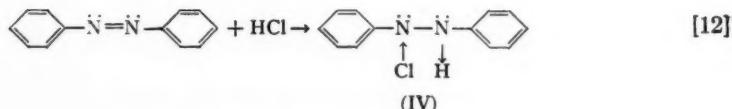


FIG. 5. Concentration-dependence of HCl catalysis plotted according to equation [11].

A plausible mechanism for the catalysis by undissociated HCl involves protonation, coupled with simultaneous co-ordination of  $\text{Cl}^-$ , to give an intermediate (IV), analogous to (III), in which the role of the solvent molecule is effectively assumed by  $\text{Cl}^-$ .



A similar mechanism may account for the combined catalytic effect of  $\text{H}^+$  and thiourea on the *cis-trans* isomerization of azobenzene, observed by Schulte-Frohlinde (2). This has the kinetic form,  $k_{\text{cat}} = [\text{H}^+] [\text{thiourea}]$  and may involve a reaction analogous to equation [12] between azobenzene and the conjugate acid of thiourea.

It is also of interest that the above pattern of catalytic effects for  $\text{HClO}_4$  and HCl resembles that found by Nozaki and Ogg (12) for the *cis-trans* isomerization of maleic acid. In the latter case also a mechanism involving simultaneous co-ordination of  $\text{H}^+$  and  $\text{Cl}^-$  (although not at adjacent positions) was proposed to account for the higher activity of HCl. Analogous mechanisms have also been proposed (13, 14) for the catalysis by secondary amines of the *cis-trans* isomerization of diethyl and dimethyl maleate.

#### Cupric Salts

Figure 6 depicts the catalytic effect due to cupric perchlorate. The kinetic dependence of  $k_{\text{cat}}$  on the cupric perchlorate concentration is greater than first order (approximately 1.5) implying some contribution from a path involving more than one  $\text{Cu}^{++}$  ion. As for  $\text{H}^+$ , it seems plausible to interpret the catalytic effect of  $\text{Cu}^{++}$  in terms of a mechanism involving co-ordination of  $\text{Cu}^{++}$  with the azo nitrogen atoms to give intermediates analogous to (III). The significance of the higher order path is not clear but a plausible interpretation is in terms of a complex, azobenzene.2 $\text{Cu}^{++}$ , in which  $\text{Cu}^{++}$  ions are

co-ordinated to both N atoms of the azobenzene molecule. The existence of an analogous cuprous complex of azomethane (azomethane.2Cu<sup>+</sup>) has been reported (15).

A similar complex, involving simultaneous co-ordination of H<sup>+</sup> and Cu<sup>++</sup> with the two N atoms of azobenzene, may account for the unexpected and very marked enhancement of the catalytic activity of cupric perchlorate by perchloric acid shown in Fig. 7. Over a considerable range of concentrations the combined effect of the two catalysts is much greater than the sum of their separate effects and the predominant contribution to  $k_{\text{cat}}$  is of the kinetic form,  $k [H^+] [Cu^{++}]$ , implying a catalytic path involving H<sup>+</sup> and Cu<sup>++</sup> simultaneously.

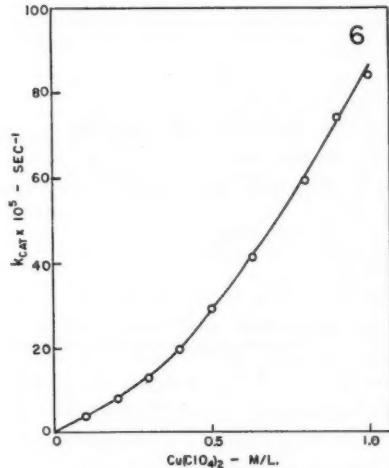
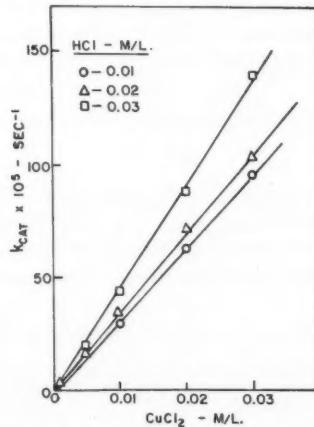


FIG. 6. Catalytic effect of cupric perchlorate in 50 mole% EtOH at 60°.

FIG. 7. Combined catalytic effects of cupric perchlorate and perchloric acid in 50 mole% EtOH at 60°.

Because of solubility limitations the effect of CuCl<sub>2</sub> in aqueous ethanol could be examined only in the presence of HCl. The results are shown in Fig. 8 and again reveal a



Catalytic effect of cupric chloride in 50 mole% EtOH at 60°.

tendency, although less marked than for cupric perchlorate, for the catalytic activity to be enhanced by the acid. At low HCl concentrations  $k_{cat}$  is first order in CuCl<sub>2</sub> and is much greater than for Cu(ClO<sub>4</sub>)<sub>2</sub> at comparable HClO<sub>4</sub> concentrations.

Cupric acetate in aqueous ethanol and cupric heptanoate in benzene (in each case in the presence of the corresponding acid which by itself was without effect) were also found to catalyze the isomerization reaction (Table I), but their effects were not examined quantitatively.

Co-ordination of the catalyst to the azo nitrogen atoms appears to be a common feature of all the catalytic effects described and the low catalytic activities of Co<sup>++</sup> and Ag<sup>+</sup>, relative to Cu<sup>++</sup> (Table I), may be related to their much smaller tendencies to form complexes with nitrogen ligands in general.

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## ENTROPY PRODUCTION IN A SPONTANEOUS, ADIABATIC (NON-ISOTHERMAL) CHEMICAL REACTION<sup>1</sup>

D. H. EVERETT<sup>2</sup>

### ABSTRACT

When a chemical reaction occurs spontaneously and isothermally the loss of useful work is equal to the decrease in free energy of the system. If the same reaction, supposed for example to be exothermic, occurs adiabatically the temperature rises and the system can be used as a source of heat to operate a heat engine: as heat is withdrawn the temperature of the system falls and eventually returns to its initial value. Part of the free energy of the reaction has been recovered as useful work, part lost in the spontaneous irreversible step. Expressions are derived for the loss of useful work and the entropy production in the adiabatic irreversible step, and it is shown that the work lost is equal to  $T_0 \times$  (entropy produced) where  $T_0$  is the temperature of the surroundings. Some consequences of these ideas in relation to the definition of the efficiency of internal combustion engines are considered briefly.

When a chemical reaction proceeds spontaneously under isothermal conditions the irreversible production of entropy in a finite change ( $\Delta_t S$ ) is related both to the "loss of useful work" and to the "decrease in free energy" (1). For a reaction which proceeds spontaneously at a temperature  $T$ ,

$$[1] \quad T\Delta_t S = \Delta W(\text{rev.}) - \Delta W(\text{irrev.}) = -\Delta F,$$

where  $\Delta W(\text{rev.})$  is the work which can be obtained if the process takes place reversibly and  $\Delta W(\text{irrev.})$  the work done by the system in an irreversible change between the same initial and final states.  $F$  is the Helmholtz free energy.

However, as pointed out by Prigogine and Defay (2), these equations cannot be applied immediately to a non-isothermal process, and a more general relationship involves the affinity of reaction (A). For an infinitesimal process:

$$[2] \quad Td\xi S = Ad\xi,$$

where

$$[3] \quad A = -(\partial F / \partial \xi)_{T,V}$$

and  $\xi$  is the extent of reaction.

In practice, we often have to deal with reactions which occur more or less adiabatically (e.g. in an internal combustion engine) so that it is instructive to see whether an equation of the form [1] can be derived for this case, and whether Prigogine and Defay's objection to this equation can be overcome.

Consider, for the sake of simplicity, an exothermic reaction



whose equilibrium position lies far to the right. We start with 1 mole of A at a temperature  $T_0$  (state  $\alpha$ ), and allow it to react spontaneously at constant volume in an adiabatic container, whose heat capacity is negligible compared with that of A or B. The final equilibrium state of the system ( $\beta$ ) is one in which  $\xi_e$  moles of A have reacted to form

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B, while the temperature has risen from  $T_0$  to  $T_1$ . Again, for simplicity, we suppose that the molar heat capacities of A and B are equal ( $c$ ) and that the heat of reaction at constant volume ( $u_{T,V}^0$ ) is independent of  $\xi$ ; it will also be independent of  $T$ . The temperature rise is then given by

$$[4] \quad T_1 - T_0 = (-u_{T,V}^0/c)\xi_e;$$

or since we suppose  $\xi_e \rightarrow 1$ ,

$$[5] \quad T_1 - T_0 = -u_{T,V}^0/c.$$

The entropy produced in this process may be obtained by integrating [2].

$$[6] \quad \Delta_1 S \text{ (chem. adiab.)} = \int_0^{t_e} \frac{A}{T} d\xi \text{ (adiabatic conditions)}$$

where

$$A = A^0 + RT \ln(1-\xi)/\xi,$$

and

$$A^0 = -u_{T,V}^0 + T s_{T,V}^0.$$

Here  $A^0$  is the standard affinity of reaction and  $s_{T,V}^0$  the standard entropy of reaction at constant volume, which is also independent of  $T$ . Remembering that  $(-u_{T,V}^0)d\xi = c dT$  under adiabatic conditions, it is readily shown that subject to the above assumptions

$$[7] \quad \Delta_1 S \text{ (chem. adiab.)} = \xi_e s_{T,V}^0 + c \ln(T_1/T_0) - R[\xi_e \ln \xi_e + (1-\xi_e) \ln(1-\xi_e)].$$

When  $\xi_e \rightarrow 1$ , this reduces to

$$[8] \quad \Delta_1 S \text{ (chem. adiab.)} = s_{T,V}^0 + c \ln(T_1/T_0).$$

The same equation is obtained from the consideration that, since the process is adiabatic, the only way in which the entropy of the system can change is by the internal production of entropy which must therefore be equal to the difference between the total entropy of final and initial states.

The system in state  $\beta$  can now be cooled to  $T_0$  (state  $\gamma$ ) in two ways. First consider reversible cooling using the system as the source of entropy working a reversible heat engine whose sink temperature is  $T_0$ : the source temperature is initially  $T_1$  but falls eventually to  $T_0$ . It may then be shown (3) that the work obtainable in this way is given by

$$[9] \quad \Delta_{\beta}^{\gamma} W \text{ (rev.)} = c(T_1 - T_0) \left[ 1 - \frac{T_0}{T_1 - T_0} \ln \frac{T_1}{T_0} \right],$$

which, from [4], reduces to

$$[10] \quad \Delta_{\beta}^{\gamma} W \text{ (rev.)} = -u_{T,V}^0 - c T_0 \ln(T_1/T_0).$$

On the other hand, if  $\beta \rightarrow \gamma$  is carried out irreversibly, i.e. by placing the system in thermal contact with the surroundings at  $T_0$  so that thermal equilibrium is established by heat conduction, then it can be shown that the entropy produced in this process,  $\Delta_1 S$  (heat cond.), is given by

$$[11] \quad \Delta_1 S \text{ (heat cond.)} = \Delta_{\beta}^{\gamma} W \text{ (rev.)} / T_0,$$

$$[12] \quad = -(u_{T,V}^0/T_0) - c \ln(T_1/T_0).$$

We now compare this two-stage path between  $\alpha$  and  $\gamma$  with the reversible isothermal path, e.g. using a van't Hoff equilibrium box, or a reversible electrochemical cell, in which the amount of work done by the system is

$$[13] \quad \Delta_a^{\gamma}W(\text{isothermal rev.}) = \int_0^{\xi_e} Ad\xi = \xi_e A^0 - RT[\xi_e \ln \xi_e + (1 - \xi_e) \ln (1 - \xi_e)].$$

Here  $\xi_e$  is the equilibrium extent of reaction at  $T_0$  rather than  $T_1$ , but since we suppose  $\xi_e \rightarrow 1$ , we do not have to elaborate the argument to take account of this. Equation [13] thus reduces to

$$[14] \quad \Delta_a^{\gamma}W(\text{isothermal rev.}) = A^0(T_0).$$

We may now identify the "loss of useful work" associated with the irreversible step  $\alpha \rightarrow \beta$  with the difference between the work done by the system in the reversible, isothermal change  $\alpha \rightarrow \gamma$ , and that done when the process follows the path  $\alpha \xrightarrow{\text{irrev.}} \beta \xrightarrow{\text{rev.}} \gamma$ .

Thus:

[Loss of useful work in adiabatic, spontaneous chemical reaction]

$$\begin{aligned} &= \Delta_a^{\gamma}W(\text{isothermal rev.}) - \Delta_b^{\gamma}W(\text{rev.}) \\ &= A^0(T_0) + u_{T,v}^0 + cT_0 \ln (T_1/T_0) \\ [15] \quad &= T_0 s_{T,v}^0 + cT_0 \ln (T_1/T_0) \end{aligned}$$

which, from [8],

$$[16] \quad = T_0 \Delta_l S \text{ (chem. adiab.)}.$$

Hence, the first number of equation [1] can be generalized to a non-isothermal process by identifying  $T$  not with the temperature of the system but with  $T_0$ , that of the surroundings. We note in passing that if both  $\alpha \rightarrow \beta$  and  $\beta \rightarrow \gamma$  are carried out irreversibly, then the entropy production (and the loss of useful work) is the same as when the process  $\alpha \rightarrow \gamma$  is allowed to proceed spontaneously at constant temperature.

As an example of the above discussion we consider the irreversible freezing of super-cooled water. This process, carried out isothermally, is a frequently quoted example in standard texts on chemical thermodynamics. When carried out adiabatically the freezing process is accompanied by a rise in temperature until the equilibrium freezing point is reached. To the approximation employed here, the fraction ( $\phi$ ) of the liquid which solidifies for a given degree of supercooling ( $T_t - T$ ) is

$$[17] \quad \phi = c(T_t - T)/\Delta_l h$$

where  $\Delta_l h$  is the heat of fusion. It is then readily shown that the entropy production in this irreversible process is

$$[18] \quad \Delta_l S = -\phi \Delta_l s + c \ln (T_t/T).$$

The entropy produced per mole of ice formed is thus

$$\begin{aligned} [19] \quad \frac{\Delta_l S}{\phi} &= -\Delta_l s + \frac{c}{\phi} \ln \frac{T_t}{T} \\ &= -\Delta_l s + \frac{\Delta_l h}{T_t - T} \ln \frac{T_t}{T} \end{aligned}$$

which tends to zero as  $T \rightarrow T_f$ .  $\Delta_t S/\phi$  is shown as a function of the degree of supercooling in Fig. 1.

The present considerations are also relevant to the question of the efficiency of internal combustion (or more generally, chemical reaction) engines. Thus the processes  $\alpha \xrightarrow{\text{irrev.}} \beta \xrightarrow{\text{rev.}} \gamma$  may be regarded as the basic steps in the operation of an "ideal internal combustion engine", and the work derivable from this series of changes is the maximum which can be obtained from any engine involving a spontaneous chemical reaction. The magnitude of this work depends not only on the heat of reaction, but also upon the

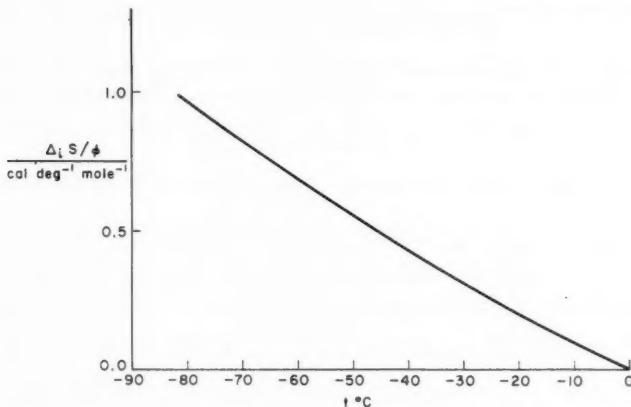


FIG. 1. Entropy production per mole of ice formed when water cooled to  $t^\circ$  C freezes spontaneously under adiabatic conditions.

heat capacities of the components: it therefore takes a much more specific account of the nature of the chemical reaction than do other treatments. In discussions of the Otto and Diesel cycles, for example, the only characteristic of the reaction which enters specifically is the heat of reaction. Conventionally, the efficiency of an internal combustion engine may be defined in relation to the heat of reaction

$$[20] \quad \theta_H = \frac{\Delta_\beta^\gamma W(\text{rev.})}{(-u_{T,V}^0)} = 1 - \frac{T_0}{T_1 - T_0} \ln \frac{T_1}{T_0} = 1 - \left( \frac{cT_0}{-u_{T,V}^0} \right) \ln \left[ 1 + \left( \frac{-u_{T,V}^0}{cT_0} \right) \right].$$

A more fundamental definition of efficiency ( $\theta_A$ ) is the ratio of the work obtained to that which could be obtained in an isothermal, reversible process (e.g. in an ideal reversible fuel cell):

$$[21] \quad \theta_A = \frac{\Delta_\beta^\gamma W(\text{rev.})}{A^0} = \frac{-u_{T,V}^0}{A^0} \left\{ 1 - \left( \frac{cT_0}{-u_{T,V}^0} \right) \ln \left[ 1 + \left( \frac{-u_{T,V}^0}{cT_0} \right) \right] \right\} = \frac{-u_{T,V}^0}{A^0} \theta_H.$$

The two efficiencies are equal when the standard entropy of reaction is zero. Alter-

native equations are

$$[22] \quad \theta_A = 1 - \frac{T_0 \Delta_i S(\text{chem. adiab.})}{A^0};$$

$$[23] \quad \theta_A = 1 - \frac{T_0}{A^0} \left[ s_{T, V}^0 + c \ln \frac{T_1}{T_0} \right].$$

$\theta_A$  may be regarded, therefore, as the ratio of the maximum fuel cell efficiency to the maximum efficiency of converting chemical energy to work via an engine involving a spontaneous chemical reaction. To illustrate the way in which the nature of the chemical reaction determines the maximum efficiency, the following table gives the results of calculations (making the approximations mentioned above) of  $\theta_H$  and  $\theta_A$  for some typical reactions, when  $T_0 = 300^\circ \text{K}$ . We notice that in the highly exothermic combination of H atoms, which because of low heat capacities involved leads to a large temperature rise, only 1% of the available "chemical energy" is lost in the irreversible step.

TABLE

Reaction	$-u_{T, V}^0$ kcal	$c_V$ cal deg $^{-1}$	$\theta_H$	$\theta_A$
$2\text{H} \rightarrow \text{H}_2$	103	5.5	0.934	0.990
$\text{H}_2 + \frac{1}{2}\text{O}_2 \rightarrow \text{H}_2\text{O}$	57.5	6.6	0.883	0.930
$\text{CH}_4 + 2\text{O}_2 \rightarrow \text{CO}_2 + 2\text{H}_2\text{O}$	191.8	17	0.914	0.915

In the above discussion, consideration has been limited to exothermic reactions. For an endothermic reaction similar arguments apply, except that  $T_1 < T_0$ , and in the step  $\beta \rightarrow \gamma$  the system is used as the sink of the heat engine whose temperature rises steadily from  $T_1$  to  $T_0$ . A chemical reaction for which  $u_{T, V}^0 = 0$  cannot form the basis of an internal combustion engine: in this case  $A^0 = T_0 \Delta_i S(\text{chem. adiab.})$  and  $\theta_A = 0$ .

In the present note, we have not elaborated the argument by taking account of incomplete reaction ( $\xi_e \neq 1$ ) or of the variation of heat of reaction with temperature, although there would be no difficulty in doing so for the purposes of more precise calculations.

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# THE INFLUENCE OF TEMPERATURE ON THE KINETICS OF CHEMISORPTION OF HYDROGEN ON ZINC OXIDE<sup>1</sup>

MANFRED J. D. LOW

## ABSTRACT

The kinetics of hydrogen adsorption by ZnO have been measured at constant pressures of 403 mm Hg over temperatures from 0° C to 257° C. Two distinct consecutive kinetic stages occur at all temperatures, each stage being precisely expressed by the Elovich equation. The rates and extents of adsorption increase in the temperature ranges 0–80° C and 110–200° C and decrease in the range 80–110° C. The change with temperature of the constants  $a$  and  $1/\alpha$  of the Elovich equation parallels changes in the amount adsorbed with temperature.

## INTRODUCTION

It has been found (1) that the kinetics of many chemisorption processes can be described by the Elovich equation,

$$(dq/dt) = a e^{-\alpha t},$$

where  $q$  is the amount of gas adsorbed at time  $t$ . The parameters  $a$  and  $\alpha$  were found (1–5) to be affected by changes in initial gas pressure and in temperature. It was suggested (2, 3, 4) that the direction of change of the parameters with temperature might be bound up with a similar change of the isobar. Previous investigations were made mainly over temperature regions corresponding to increasing or to decreasing regions of the isobar, and it was consequently thought desirable to measure chemisorption kinetics in a temperature region in which an adsorption maximum or minimum existed. The system hydrogen – zinc oxide was chosen because two maxima and one minimum were known to exist (7, 8, 9) in the chemisorption region of about 0°–300° C.

## EXPERIMENTAL DETAILS

The course of hydrogen adsorption was followed by measuring the disappearance of gas in a constant pressure system of the type described by Taylor and Strother (8). The electrolysis cell of that system was modified by addition of a water jacket in order to cool the electrolyte. The latter consisted of a concentrated solution of sodium acetate in glacial acetic acid and was electrolyzed by a current of 5–8 amps at 40–60 v a-c. Gold electrodes of  $\sim 300 \text{ mm}^2$  area, about 3 cm apart, were used. Electrolytic tank hydrogen was purified by passage over palladized asbestos, Ascarite, Drierite, and glass wool at the temperature of liquid nitrogen. Helium, used for measurement of dead space in the usual fashion, was purified by passage over charcoal at the temperature of liquid nitrogen. During an adsorption experiment the catalyst was kept at the described temperature to within  $\pm 0.1^\circ \text{C}$  by the vapor of a boiling liquid. A Wheelco Amplitrol Model 152 was used to regulate temperatures to within about 5° C during degassing. Two sets of experiments were made. The first, set A, is incomplete because experiments became irreproducible, probably due to accidental exposure of the catalyst to air. Except where specifically noted, all reference is to the data of the second set, B.

The adsorbent was prepared by decomposing zinc oxalate *in vacuo* by heating at the following schedule: 20–100° C, 1 hour; 100–200°, 1 hour; 200–300°, 1.5 hours; at 400°,

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Contribution from the Texaco Research Center, Beacon, N.Y.

4 hours; at 450°, 15 hours. Evolution of gas began at about 150°, and continued until 400° had been reached. After the 450° treatment the catalyst was cooled *in vacuo*. For set B, a 19.76-g sample of the preparation was placed in a tube which was then sealed to the adsorption system. This catalyst was degassed at 450° for 2 days, was then cooled to 300°, and exposed to hydrogen at  $\frac{1}{2}$  atm for about 30 minutes. The catalyst was then degassed at 420° C for 20 hours. This "activation" procedure was repeated twice. Residual pressures  $< 10^{-6}$  mm Hg were attained. Between runs the catalyst was degassed at 420° C overnight. The adsorbent had a nitrogen B.E.T. surface area of 16 m<sup>2</sup>/g. Experiments were made at constant pressure of 403 mm Hg.

### EXPERIMENTS, RESULTS, AND DISCUSSION

#### Kinetics of Chemisorption

At the lower temperatures the plots of  $q$  vs.  $t$  showed the characteristics of "normal" adsorption, namely a rapid adsorption at short times that quickly decelerated. Each of the  $q$ - $t$  curves of runs at the higher temperatures, however, shows a distinct "dip", or change in rate, after some 20 to 80 minutes, shown in the plots of Fig. 1. Similar dips

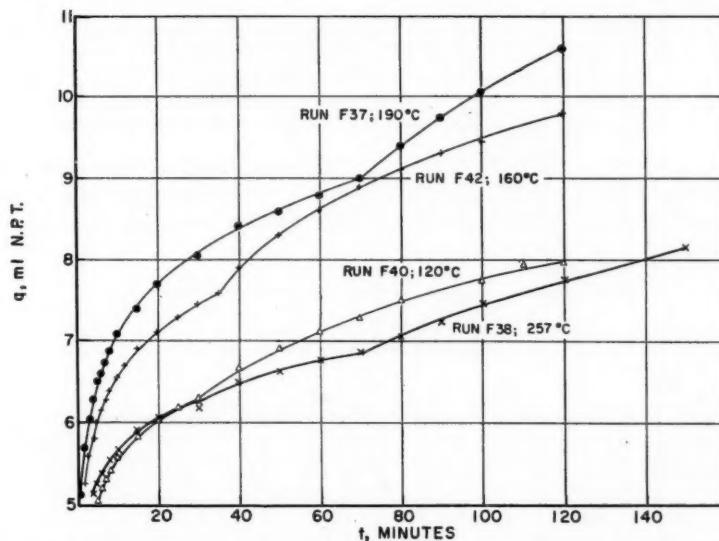


FIG. 1. Adsorption rate data: typical runs. The points of F42, F38, and F40 are displaced by 1, 4, and 5 minutes, respectively.

are noticeable in the  $q$ - $t$  data of hydrogen adsorption on ZnO of Taylor and Sickman (6) and Taylor and Strother (8). These authors drew smooth curves through the data, ignoring the dip. Indeed, on cursory examination the dips might be ascribed to experimental scatter, especially in the plots of data at the lower temperatures. However, as shown by Fig. 2, plots of  $q$  vs.  $\log_{10} t$  show the presence of two distinct kinetic stages. After some time the  $q$ - $\log_{10} t$  line changes in slope, and such discontinuities, or "breaks", are present in the data of all runs, and are also found in the  $q$ - $\log_{10} t$  plots of the data of other studies (6, 8). Each linear portion of a  $q$ - $\log_{10} t$  plot can be described by the Elovich equation (1).

*Isobars*

Plots of amounts adsorbed after a specific time,  $q_t$ , against temperature reveal the double-humped isobars first described by Taylor and Strother (8). Figure 3 shows curves

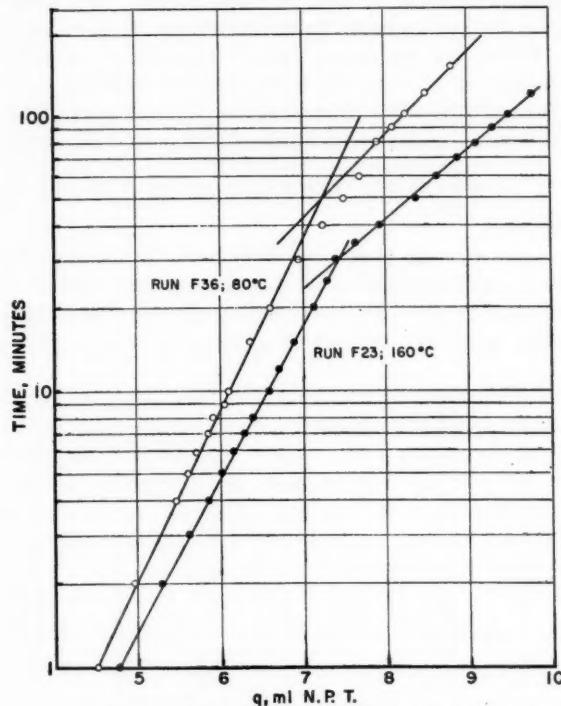


FIG. 2. Adsorption rate data: Elovich plots.

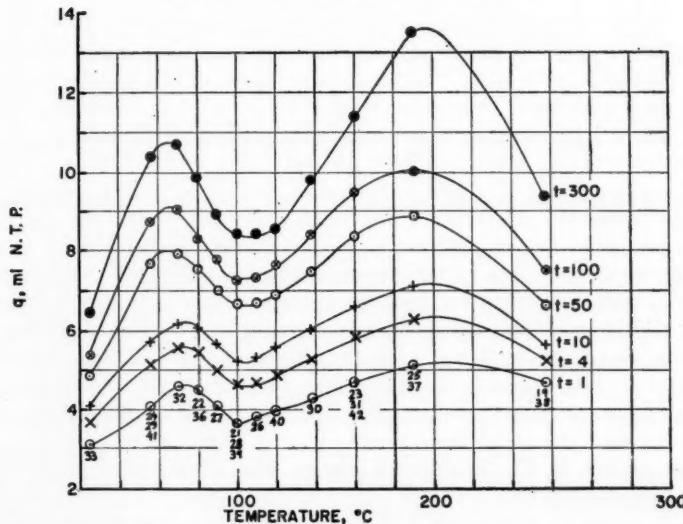


FIG. 3.  $\text{H}_2\text{-ZnO}$  isobars. The numbers next to points of the  $t = 1$  curve are those of the experiments, which were numbered consecutively in order of their execution.

representing amounts adsorbed after 1, 4, 10, 50, 100, and 300 minutes at each temperature. Adsorption maxima appear at about 70° and 200°, and a minimum appears at about 105°. Inspection of Table I reveals small temperature differences in isobar positions. Cimino, Cipollini, and Molinari (9) were able to displace the position of their isobar by about 20° by sintering their adsorbent at 900°. The relatively small differences in isobar positions of pure ZnO suggests that the maxima are not very sensitive to catalyst preparation variables, although it has been shown (9) that the structure of the isobar is severely affected by doping the ZnO.

TABLE I  
Temperatures of occurrence of the maxima and the minimum of the adsorption isobar of hydrogen on zinc oxide

Investigation*	Maximum, °C	Minimum, °C	Maximum, °C
(a) Taylor and Strother (8)	80	97	218
(b) Wicke (7)	70	100	260
(c) Cimino <i>et al.</i> (9)	50	105	—
(c, d) Cimino <i>et al.</i> (9)	70	135	190
(e) Present experiments	70	105	200
(f) Present experiments	80	110	200

- \*(a) Measured after 1000 minutes; pressure: 1 atm.
- (b) Measured after 600 minutes; pressure: 1 atm.
- (c) Measured after 900 minutes; pressure: 1 atm.
- (d) After sintering the catalyst at 900° C.
- (e) Set B measured after 300 minutes.
- (f) Set A measured after 500 minutes.

#### Effect of Temperature on Rate Constants

Values of the constants  $a$  and  $\alpha$  were calculated (10) for each linear portion of an Elovich plot, and are given graphically as functions of temperature in Figs. 4, 5, and 6.

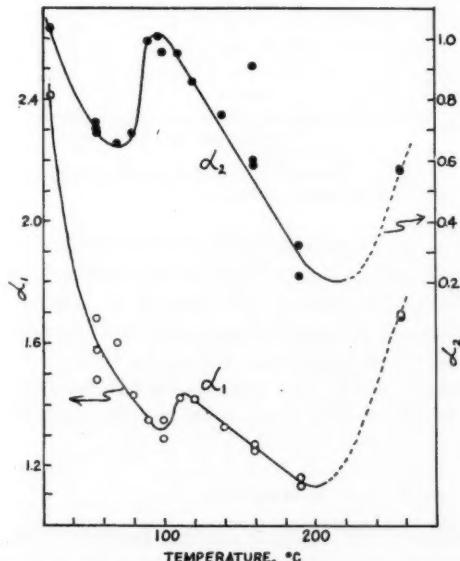


FIG. 4. The effect of temperature on  $\alpha$ .

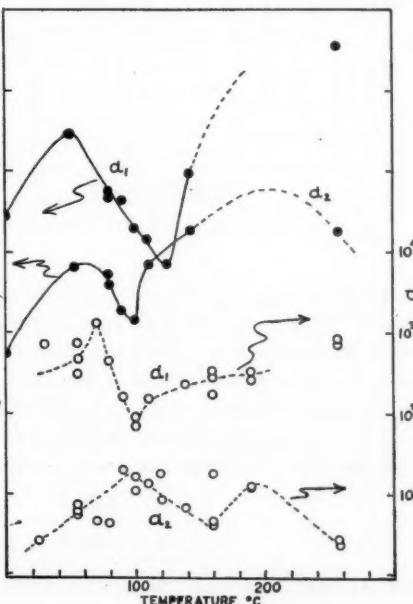


FIG. 5. The effect of temperature on  $a$ . ●, Data of set A. ○, Data of set B. The catalyst of set A consisted of 31.30 g ZnO ex oxalate.

The subscripts 1 and 2 refer to the constants for the first and second lines of Elovich plots, respectively. The structure shown by the  $\alpha$ - $T$  plots of Fig. 4 is similar but inverse of that of the isobar. The plots of Fig. 5 of the more sensitive (2, 3, 4) values of  $a$  against temperature similarly reflect the isobar structure, but show more scatter. In Fig. 5 the lower two curves formed by open circle refer to the data of set B, while the upper two curves refer to the incomplete set A, shown here to illustrate the trends in  $a$ - $T$  relations. The ratio of the rate of the second kinetic process to that of the first process is  $\alpha_1/\alpha_2$ . Figure 6 shows the  $\alpha_1/\alpha_2$ - $T$  relation: undulations similar to those of the isobar are apparent, so that the effect of temperature on the second kinetic process is greater than that on the first process. Figure 7 shows values of the co-ordinates  $q_b$  and  $t_b$  of the break

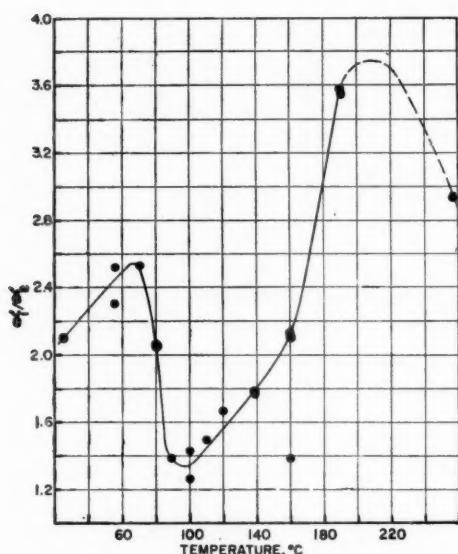


FIG. 6. The effect of temperature on  $(\alpha_1/\alpha_2)$ .

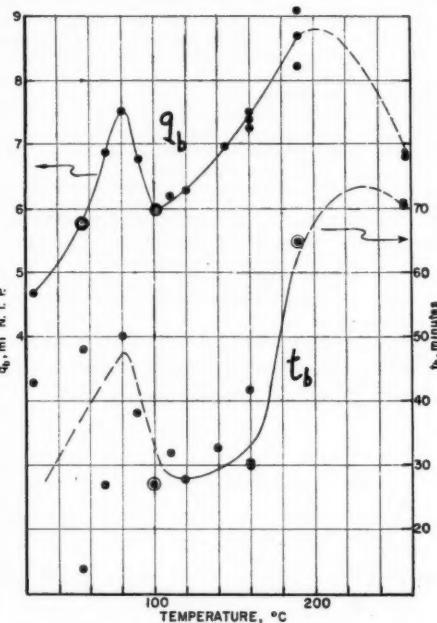


FIG. 7. The variation of the co-ordinates of the break with temperature.

of Elovich plots at various temperatures. The  $q_b$ - $T$  plot shows structures similar to that of the isobar. The  $t_b$ - $T$  plot shows some variations but, because of the exponential effect of scatter of  $a$  values on those of  $t_b$ , the trends are not well defined. In general, then, in the present system of  $H_2$ -ZnO, the rates of adsorption vary with temperature in a fashion similar to the variation of the extents of adsorption after long times.

It is obvious that the temperature dependencies of the rate parameters can be more complex than had been previously believed. Earlier studies (1-4) show simple relations

$$\alpha = A + B/T$$

$$\log a = C + D/T$$

$A, B, C, D = \text{constants}$

to hold over ranges of temperatures covering about  $200^\circ \text{C}$ . Such studies, however, had been made in a temperature region of continuously increasing or decreasing adsorption. Such linear equations can be constructed for the present data. The constants  $\alpha_1$  and  $\alpha_2$

over the range 120-190° C, for example, vary inversely with temperature. In view of the undulations of the isobar, however, such equations are pointless in this case. Similarly pointless are calculations of activation energies of adsorption, particularly in the region 80-110° C, where negative activation energies are obtained. By analogy one may expect similar undulant variations of rate parameters with temperature to occur with the adsorption of hydrogen on iron synthetic ammonia catalyst (11), the only other system known to exhibit the double-humped isobar. Also, a consistent reversal of temperature coefficients in the vicinity of a normal adsorption isobar maximum seems plausible. However, because no adequate general explanation of these phenomena is apparent, the sign and magnitude of the temperature coefficients in both the ascending and the descending portions of the isobar cannot be predicted.

#### *The Effect of Continuously Changing Temperature*

Taylor and Liang (12) found that if the temperature of a sample of ZnO almost saturated with hydrogen was suddenly increased, a desorption followed by a readsorption of gas occurred. When the temperature was decreased, increased adsorption was found. It was thought of interest to perform several experiments in order to determine if similar results would be obtained when (a) the temperature was changed relatively slowly and in continuous fashion; (b) the adsorbent was in a state relatively far removed from complete coverage.

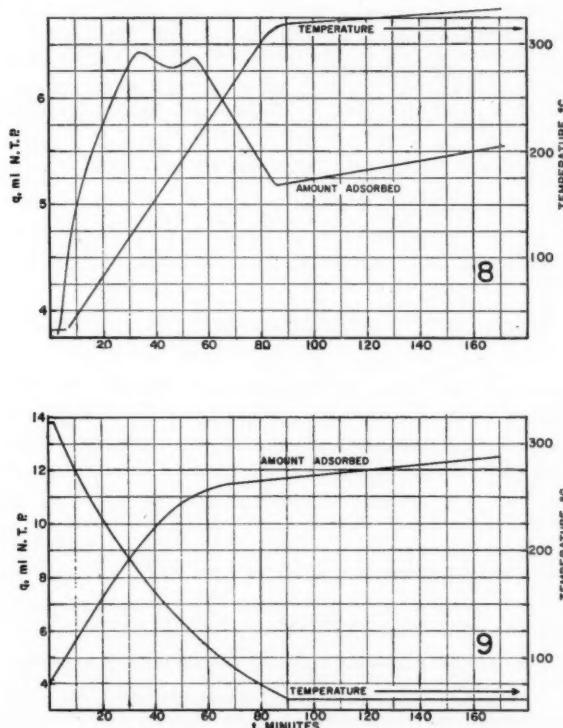


FIG. 8. The effect of continuously increasing temperature.  
 FIG. 9. The effect of continuously decreasing temperature.

Run F34 was started in normal fashion, with the catalyst degassed, at a temperature of 33° C. However, instead of keeping the temperature constant as in a normal run, the temperature was raised at a rate of about 4°/minute to about 314° C. Readings were made every minute except after 85 minutes. The numerous  $q$  data as well as the prevailing furnace temperature are shown in Fig. 8 as smoothed plots as functions of time. Adsorption ceases to increase at about 130°, and a continual decline in  $q$  is found after about 205° C. The significance of the small dip in the  $q-t$  curve at about 180° is not clear: the decline in  $q$  between 140° and 180° is only about 0.15 ml. Further, it may be expected that the temperature of the catalyst will not be uniform and will be at a slightly lower temperature than that of the furnace.

Run F35 was started at 323° C in normal fashion, but the temperature was allowed to fall to 69° C. In Fig. 9 the smoothed  $q-t$  plot of the numerous data shows continuous increase in adsorption with time. The rate of adsorption declines slowly and becomes roughly constant in the constant temperature region after 100 minutes. The results of the two experiments are thus comparable to those of the experiments of Taylor and Liang. Apparently quite drastic departures from the techniques of those authors will not bring about significantly different results.

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# THE THIRD LAW ENTROPY AND STRUCTURE OF IRON PENTACARBONYL<sup>1</sup>

A. J. LEADBETTER<sup>2</sup> AND J. E. SPICE<sup>3</sup>

## ABSTRACT

The heat capacity of solid and liquid iron pentacarbonyl has been measured from 20° to 290° K. The heat of fusion was also measured and found to be  $3161 \pm 3$  cal/mole. From an investigation of the change of temperature of the sample during melting the triple point of iron pentacarbonyl was estimated to be 253.15° K and the purity of the sample 99.9 mole%. An anomalous absorption of energy amounting to 4.8 cal/mole was observed at about 230° K; this is shown to be due to an unknown impurity in the sample. The vapor pressure of the liquid was measured in the vicinity of room temperature and from these results the heat of vaporization at 25° C was estimated to be  $9.1 \pm 0.1$  kcal/mole.

The entropy of iron pentacarbonyl as an ideal gas at 1 atm pressure and 25° C computed from the thermal measurements is  $106.4 \pm 0.8$  cal/mole deg. Comparison of this quantity with values calculated from spectroscopic data indicates that the iron pentacarbonyl molecule has the form of a trigonal bipyramidal rather than that of a square pyramid.

## INTRODUCTION

The iron pentacarbonyl molecule, one of the few of type  $AX_5$ , might on general grounds be either a trigonal bipyramidal or a square pyramid. An electron diffraction study (1) indicated a trigonal bipyramidal structure but this does not appear to be consistent with the reported dipole moment of 0.8 Debye (2). An attempt has been made to use nuclear resonance techniques to determine the structure but the results were inconclusive (3).

Many spectroscopic investigations have been reported but the photosensitivity of iron pentacarbonyl has made it difficult to obtain the Raman spectrum which is necessary for an unambiguous frequency assignment. However, the weight of spectroscopic evidence favors the bipyramidal structure (3, 4, 5, 6) although O'Dwyer (7) has recently claimed that his infrared results can best be interpreted on the basis of the square pyramid structure.

It has thus not been possible to establish conclusively the structure of the iron pentacarbonyl molecule from spectroscopic data alone. A comparison of the Third Law entropy with the statistical value calculated on the basis of the two possible structures and the corresponding frequency assignments might therefore help to decide between the two structures.

## EXPERIMENTAL

### *The Material*

We are grateful to the Mond Nickel Co. Ltd. for supplying the sample of iron pentacarbonyl. It was supplied in the form of the pure liquid, and an analysis of the freezing curve by the method of Taylor and Rossini (8) indicated the purity to be 99.9 mole%. The sample was therefore used without further purification; a subsequent study of the melting curve confirmed the above value for the purity.

### *The Calorimetric Method*

The cryostat contained a miniature hydrogen liquefier of the type used by Jones<sup>4</sup>

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<sup>4</sup>We are grateful to Professor G. O. Jones for his help while we were designing and constructing the liquefier.

(9). The calorimetric measurements were made with a conventional vacuum adiabatic calorimeter by standard methods. All of the measurements were made with a White double potentiometer. Time of energy input was determined with a Venner mechanical stop clock, the solenoid switching mechanism of which was coupled directly to the switch controlling the heater current. The clock was calibrated by comparison with the B.B.C. time signals. The platinum resistance thermometer was calibrated on the International Temperature Scale above 90° K and on the thermodynamic scale below this temperature. The calorimetric apparatus and the establishment of the temperature scale below 90° K will be fully described elsewhere (10).

The copper calorimeter vessel, weighing 240 g, was filled with 0.5906 mole of sample in a dimly lit, dry atmosphere. It was sealed by pinching shut and sealing with solder a short length of thin-walled nickel tubing previously soldered into the neck of the vessel. The heat capacity of the calorimeter amounted to 17% of the total at 20° K and to 39% at 290° K. Temperature increments of between 4° and 8° were generally used except in the region of 230° K, where smaller increments were used in order to investigate the anomalous energy absorption.

#### *The Vapor Pressure Measurements*

The vapor pressure of the liquid was measured between 20° and 33° C using a mercury manometer of 17-mm-bore tubing. Pressures were measured using a comparator telescope and a glass scale, etched in 0.5-mm divisions, which was freely suspended between the arms of the manometer; the accuracy of pressure measurement is estimated to be  $\pm 0.05$  mm. The temperature of the sample was maintained constant to  $\pm 0.02$ ° for each pressure determination, by means of a water thermostat. The vapor space was always maintained at a slightly higher temperature than the liquid. Temperatures were measured to  $\pm 0.02$ ° with a mercury-in-glass thermometer, the ice point reading of which had been found correct within these limits. In order to prevent photochemical decomposition light was excluded from these portions of the apparatus containing the iron pentacarbonyl; as a check against possible decomposition, measurements were made after both warming and cooling the sample.

## RESULTS

#### *The Heat Capacity*

The experimental results are given in Table I (the ice point was taken as 273.16° K and the calorie as 4.1840 absolute joules). The maximum deviation of any point from a smoothed curve is 0.4% and the average deviation  $\pm 0.1\%$ , except in the anomalous region where the measurements were somewhat less precise. The accuracy of the results is estimated to be  $\pm 0.5\%$  for  $20^\circ \text{K} < T < 50^\circ \text{K}$  and  $\pm 0.3\%$  for  $T > 50^\circ \text{K}$ . The heat capacity curve shows a quite regular behavior except for a very small peak at about 230° K, associated with the absorption of an "extra" energy of 4.8 cal/mole over a narrow temperature range. A preliminary investigation of the heat capacity of iron pentacarbonyl, made in this laboratory by McGowan (11), had indicated the presence of a much larger anomaly in the heat capacity curve. It was shown in the present work, by determination of the heat capacity after cooling through the anomalous region at different rates and to different temperatures, that the size of the anomaly was independent of the previous history of the sample. The data obtained on the apparent anomaly in the two investigations are compared in Table II.  $T_{\max}$  is the temperature at which the heat capacity in the anomalous region reaches its maximum value. The amount of impurity in each specimen was estimated from the depression of the melting point.

TABLE I  
The heat capacity of  $\text{Fe}(\text{CO})_5$

Temp. (° K)	$C_p$ (cal/mole deg)	Temp. (° K)	$C_p$ (cal/mole deg)
22.59	6.66	213.84	40.89
27.47	9.39	217.24	41.09
38.15	13.77	219.29	41.57
44.19	15.76	220.42	41.57
49.32	17.20	222.58	41.60
53.86	18.20	223.61	41.87
59.91	19.51	225.84	42.60
67.30	20.86	226.81	42.53
73.96	21.83	227.80	43.53
85.07	23.42	228.57	43.35
88.55	23.84	229.33	43.36
99.21	25.01	229.97	44.02
104.33	25.72	230.13	43.63
109.25	26.26	230.90	42.67
116.83	27.48	232.07	42.72
126.98	29.00	233.11	43.28
136.62	30.39	233.49	43.45
145.87	31.80	236.24	43.72
154.78	33.22	236.59	43.58
158.52	33.98	241.61	45.11
163.34	34.47	248.14	53.47
166.96	35.15	253.15	Fusion
169.65	35.34	258.58	55.86
175.20	36.27	269.33	56.10
183.20	37.18	275.35	56.57
191.05	38.11	281.35	56.82
198.74	39.06	287.33	56.89
206.32	39.93		

TABLE II  
The apparent anomaly in  $\text{Fe}(\text{CO})_5$  at 230° K

$T_{\max}$ (° K)	$\Delta H$ (cal/mole)	Impurity (mole%)	
$229.9 \pm 0.1$	$4.84 \pm 0.05$	0.1	This work
$229.7 \pm 0.3$	124 $\pm 1$	3.4	McGowan

Within the limits of experimental uncertainty the size of the anomaly is directly related to the amount of impurity in the specimen, showing that the anomaly must be caused in some way by the impurity and is not an intrinsic property of pure iron pentacarbonyl. The most probable explanation of the anomaly is that it is due to the melting of an eutectic mixture present in a small amount. Unfortunately, the nature of the impurity is not known but the most likely impurities in iron pentacarbonyl are nickel carbonyl and  $\text{Fe}_2(\text{CO})_9$  formed in the photochemical decomposition of the pentacarbonyl. Since both samples were obtained from the same source it seems unlikely that they initially contained such differing amounts of impurity and this would suggest that  $\text{Fe}_2(\text{CO})_9$  is the most likely impurity. However, without additional experimental data further speculation would appear to be of little value. In addition, it should be noted that the entropy associated with the anomaly (0.02 cal/mole deg) is quite negligible in the determination of the standard entropy.

*The Triple Point and Heat of Fusion*

The equilibrium temperatures as a function of the fraction of the sample melted are shown in Table III. From these results the calculated triple point of iron pentacarbonyl is 253.15° K.

TABLE III  
The melting point of  $\text{Fe}(\text{CO})_5$

% Melted	$T^\circ \text{K}$
31	253.018
50	253.062
67	253.084
84	253.097
100	253.11

NOTE: Impurity: 0.1 mole%. Triple point: 253.15° K.

The heat of fusion was determined in the usual manner, the premelting energy being included in the heat of fusion. Two determinations gave respectively 3158.7 and 3162.6 cal/mole, or a mean value of  $3161 \pm 3$  cal/mole. The only previously published value for the heat of fusion is  $3250 \pm 40$  cal/mole reported by Mittasch (12).

*The Vapor Pressure*

The experimental results are given in Table IV. Pressures are expressed in terms of the height of a column of mercury under standard gravity at 0° C. The results may be represented within their experimental uncertainty by the formula

$$\log P \text{ (mm)} = 8.514 - (2105/T)$$

as is shown in Table IV.

TABLE IV  
The vapor pressure of  $\text{Fe}(\text{CO})_5$

Temp. (° K)	$P_{\text{obs}}$ (mm)	$P_{\text{calc}}$ (mm)	Temp. (° K)	$P_{\text{obs}}$ (mm)	$P_{\text{calc}}$ (mm)
293.47	21.95	21.90	301.44	34.00	33.89
294.36	23.01	23.02	302.71	36.38	36.25
295.99	25.38	25.21	302.91	36.65	36.64
296.94	26.45	26.56	303.48	37.88	37.77
297.98	28.05	28.12	304.01	38.70	38.83
298.30	28.68	28.62	305.24	41.37	41.41
299.60	30.56	30.70	305.30	42.73	41.53
300.26	31.67	31.82	306.32	43.60	43.78

The above formula has been compared with vapor pressure data reported by Dewar and Jones (13) between  $-7^\circ$  and  $78^\circ$  C, Eyber (14) between  $-15^\circ$  and  $20^\circ$  C, and Trautz and Badstübner (15) between  $46^\circ$  and  $104^\circ$  C. The results of Dewar and Jones appear to be too high below about  $40^\circ$  C, while those of Eyber are in excellent agreement with the present work. The results of Trautz and Badstübner are higher by about 1% at  $46^\circ$  C and the deviation increases with temperature. This, however, may only represent the inadequacy of a two-constant expression for  $\log P$  over any but a restricted temperature range.

The heat of vaporization at  $25^\circ$  C was calculated by means of the Clausius-Clapeyron equation, the Berthelot equation of state being used to correct for gas imperfection. The

values of the critical constants used were  $T_c = 560^\circ \text{ K}$  and  $P_c = 29.6 \text{ atm}$  (13). The heat of vaporization of iron pentacarbonyl was found to be  $9.6 \pm 0.1 \text{ kcal/mole}$ .

### DISCUSSION

#### *The Third Law Entropy of $\text{Fe}(\text{CO})_5$*

The computation of the entropy of iron pentacarbonyl as an ideal gas at 1 atm pressure and  $25^\circ \text{ C}$  is summarized in Table V. The extrapolation of the heat capacity from  $22.59^\circ$  to  $0^\circ \text{ K}$  was carried out by means of a Debye function with 18 degrees of freedom and  $\Theta = 155^\circ \text{ K}$ .

TABLE V  
The Third Law entropy of  $\text{Fe}(\text{CO})_5$

	cal/mole deg
$\Delta S$ ( $0^\circ$ to $22.59^\circ \text{ K}$ ) Debye extrapolation	$2.7 \pm 0.2$
$\Delta S$ ( $22.59^\circ$ to $253.15^\circ \text{ K}$ ) solid	$56.3 \pm 0.2$
$\Delta S_{253.15}^{298.16}$ ( $3161/253.15$ ) fusion	$12.49 \pm 0.02$
$\Delta S$ ( $253.15^\circ$ to $298.16^\circ \text{ K}$ ) liquid	$9.26 \pm 0.03$
$\Delta S_{298.16}^{298.16}$ ( $960/298.16$ ) vaporization	$32.2 \pm 0.3$
Entropy of real gas at $28.4 \text{ mm}$ and $298.16^\circ \text{ K}$	$112.9 \pm 0.7$
$\Delta S_{\text{compression}} R \ln (28.4/760)$	$-6.53 \pm 0.01$
Correction for gas imperfection	$0.01$
Entropy of the ideal gas at $1 \text{ atm}$ and $298.16^\circ \text{ K}$	$106.4 \pm 0.8$

#### *The Statistical Entropy of $\text{Fe}(\text{CO})_5$*

The standard entropy of iron pentacarbonyl has been calculated from spectroscopic data by standard methods, using the rigid rotator - harmonic oscillator approximation. The values of the fundamental constants were taken from the tables of Kaye and Laby (16).

The computation was carried out for both the trigonal bipyramidal model (symmetry  $D_{3h}$ ) and the square pyramid model (symmetry  $C_4v$ ) and in both cases the following interatomic distances were used (1): Fe—C,  $1.84 \text{ \AA}$  and C—O,  $1.15 \text{ \AA}$ ; the Fe—C—O groups were assumed linear. The  $D_{3h}$  model was precisely that proposed by Ewens and Lister (1) on the basis of their electron diffraction studies, while for the  $C_4v$  model the four equivalent CO groups were assumed coplanar with the Fe atom and the remaining CO group perpendicular to the plane. This is a reasonable assumption since the C—Fe—C angle would not be expected to differ greatly from  $180^\circ$  and numerical values of entropy are not sensitive to small changes in bond angles. In fact, the difference in the moments of inertia of the  $D_{3h}$  and  $C_4v$  models contributes less than  $0.01 \text{ cal/mole deg}$  to the difference in the rotational entropies of the two structures; almost the whole difference is due to the change of symmetry number from 6 to 4.

A serious deficiency in the frequency assignments of King and Lippincott (4, 5), Murata and Kawai (6), Edgell and Wilson (see ref. 5), and O'Dwyer (7) is the lack of experimental data on the low frequency C—Fe—C deformation modes, to which the thermodynamic properties at normal temperatures are most sensitive. Only one of these fundamentals was directly observed, the remainder being obtained from infrared combination bands or by comparison with similar molecules. Very recently, however, Cotton Danti, Waugh, and Fessenden (3) have reported the observation of these low frequency fundamentals. They conclude that these and other (unpublished) results at higher frequencies are more consistent with the  $D_{3h}$  than the  $C_4v$  model and have accordingly

assigned the observed fundamentals on this basis. The various assignments proposed for the C—Fe—C deformation modes on the basis of both molecular models are given in Table VI, where the numbering is taken from the original papers.

TABLE VI  
C—Fe—C deformation frequencies

$D_{3h}$					$C_{4v}$			
Symmetry	Frequency ( $\text{cm}^{-1}$ )				Symmetry	Frequency ( $\text{cm}^{-1}$ ), O'Dwyer		
	King and Lippincott	Murata and Kawai	Edgell and Wilson	Cotton <i>et al.</i>				
$\nu_9$	$A_2''$	100	100	115	93	$\nu_6$	$A_1$	79
$\nu_{14}$	$E'$	110	110	92	72	$\nu_{11}$	$B_1$	185
$\nu_{15}$	$E'$	100	63	102	104	$\nu_{13}$	$B_2$	146
$\nu_{18}$	$E''$	110	95	110	112	$\nu_{19}$	$E$	103
						$\nu_{20}$	$E$	71

The vibrational entropy for the  $D_{3h}$  model has been calculated using each of the proposed frequency assignments, first as published and then corrected to include the observed low frequency fundamentals reported by Cotton *et al.* For the  $C_{4v}$  model O'Dwyer's assignment has first been used to calculate the vibrational entropy, but in order to provide a fair comparison of the two models it is necessary to correct his assignment to incorporate the new spectroscopic results for the low frequency fundamentals and calculate the entropy on this basis also. This may be done most reasonably by assigning the observed fundamentals to  $\nu_6$  ( $93 \text{ cm}^{-1}$ ),  $\nu_{13}$  ( $112 \text{ cm}^{-1}$ ),  $\nu_{19}$  ( $104 \text{ cm}^{-1}$ ), and  $\nu_{20}$  ( $72 \text{ cm}^{-1}$ ) but it must be emphasized that such an assignment does not appear to be consistent with the spectroscopic results. The results of the entropy calculations are summarized in Table VII, the final column contains the entropies calculated using the frequency assignments corrected to incorporate the observed values for the low frequency fundamentals.

TABLE VII  
The statistical entropy of  $\text{Fe}(\text{CO})_5$

Model	Moments of inertia ( $\text{g cm}^2 \times 10^{40}$ )		$S^\circ_{\text{trans+rot}}$ (cal/mole deg)	Frequency assignment	$S^\circ_{\text{vib}}$ (cal/mole deg)	$S^\circ$ (cal/mole deg)	$S^\circ_{\text{corr}}$ (cal/mole deg)
	$I_A$	$I_B = I_C$					
$C_{4v}$	1220	861	69.5 <sub>4</sub>	O'Dwyer	35.5 <sub>2</sub>	105.1	105.2
$D_{3h}$	915	1067	68.9 <sub>0</sub>	King and Lippincott*	35.4 <sub>7</sub>	104.4	106.0
				Murata and Kawai	34.5 <sub>2</sub>	103.4	102.6
				Edgell and Wilson	36.0 <sub>1</sub>	104.9	106.1
Third Law entropy							$106.4 \pm 0.8$

\*The values of  $S^\circ$  and  $-(F^\circ - E_g^\circ)/T$  quoted by King and Lippincott (4) are too high at all temperatures by 1.9 cal/mole deg.

The comparison of the Third Law entropy with the statistical value, calculated using the new results of Cotton *et al.* for the C—Fe—C deformation frequencies, provides strong support for the  $D_{3h}$  rather than the  $C_{4v}$  model for the iron pentacarbonyl molecule. In view of the evidence from electron diffraction and spectroscopic studies, which alone were not conclusive, and the new evidence presented here from thermodynamic studies, it can now be concluded with reasonable certainty that the structure of the iron pentacarbonyl molecule is a trigonal bipyramidal.

The above comparison cannot help to resolve the details of the frequency assignment since the entropies calculated on the basis of the assignments of King and Lippincott and Edgell and Wilson are very close, while the frequency assignments differ considerably in detail. However, it can be concluded that the assignment proposed by Murata and Kawai based on the same experimental data as that of King and Lippincott, must be seriously in error.

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## NOTES

**CONFIGURATION OF GLYCOSIDIC LINKAGES IN OLIGOSACCHARIDES**  
**VIII. SYNTHESIS OF  $\alpha$ -D-MANNOPYRANOSYL- AND  $\alpha$ -L-RHAMNOPYRANOSYL-**  
**DISACCHARIDES BY THE KÖNIGS-KNORR REACTION\***

P. A. J. GORIN AND A. S. PERLIN

**6-O- $\beta$ -D-Mannopyranosyl-D-glucose** was required for studies on oligosaccharide structure. A synthesis of the octa-*O*-acetyl derivative of this disaccharide via the Königs-Knorr reaction (1) has been reported by Talley, Reynolds, and Evans (2), who condensed 2,3,4,6-tetra-*O*-acetyl- $\alpha$ -D-mannopyranosyl bromide with 1,2,3,4-tetra-*O*-acetyl- $\beta$ -D-glucose in the presence of silver oxide. The procedure of these earlier workers has now been repeated, and the disaccharide fraction produced was deacetylated and isolated by column chromatography on cellulose (3). The amorphous material, which contained a major and a minor component (chromatographic evidence), showed an unexpectedly strong dextrorotation ( $[\alpha]_D +64^\circ$ ). Examined by the periodate oxidation procedure described in Part I of this series (4), it yielded a product ( $[\alpha]_D +63^\circ$ ) which corresponded in optical rotation much more closely to that (I, free trialdehyde form) given by (1  $\rightarrow$  6)- $\alpha$ -D-aldohexopyranosyl disaccharides (for example, No. 1, Table I), than by the  $\beta$ -D-anomers

TABLE I  
 Specific rotations of the products obtained by periodate oxidation of disaccharides and methyl glycosides

Compound	$[\alpha]_D$	$[\alpha]_D$ <sup>a</sup> oxidized	Ref.
1. 6-O- $\alpha$ -D-Glucopyranosyl-D-glucose	+120°	+85°	4
2. 6-O- $\alpha$ -D-Mannopyranosyl-D-glucose	+75°	+85°	b
3. 6-O- $\beta$ -D-Glucopyranosyl-D-glucose	+8°	+109°	4
4. 6-O- $\alpha$ -D-Mannopyranosyl-D-mannose	+57°	+82°	b
5. 6-O-(6-Deoxy- $\alpha$ -L-mannopyranosyl)-D-glucose	-0.1°	-110°	b
6. 6-O-(6-Deoxy- $\alpha$ -D-galactopyranosyl)-D-glucose <sup>c</sup>	+125°	+100°	b
7. 6-O-(6-Deoxy- $\beta$ -D-glucopyranosyl)-D-glucose <sup>d</sup>	-6°	-30°	b
8. Methyl 6-deoxy- $\alpha$ -L-mannopyranoside	-63°	-143°	13
9. Methyl 6-deoxy- $\beta$ -L-galactopyranoside	+14°	+89°	13
10. Methyl 6-deoxy- $\beta$ -D-glucopyranoside	-55°	-88°	13

<sup>a</sup>Based on the assumption that the compound on oxidation yields the corresponding di- or tri-aldehyde in quantitative yield (4).

<sup>b</sup>Present work.

<sup>c</sup>Prepared in low yield as a chromatographically pure syrup from 6-O- $\alpha$ -D-galactopyranosyl-D-glucose, via a series of reactions utilized commonly for preparation of  $\omega$ -deoxy sugars and derivatives (cf. (28)), i.e., tritylation, acetylation, de tritylation, tosylation, iodination, reduction, deacetylation; intermediate products were not isolated.

<sup>d</sup>Obtained as the  $\beta$ -hepta-*O*-acetate (m.p. 175-176° C;  $[\alpha]_D^{25} -2^\circ$  (c, 1.4, chloroform). Calculated for  $C_{14}H_{20}O_{17}$ : C, 50.32%; H, 5.85%. Found: C, 50.35%; H, 5.93%) by condensation of 2,3,4-tri-*O*-acetyl(6-deoxy- $\alpha$ -D-glucopyranosyl)-bromide ((m.p. 152-155° C;  $[\alpha]_D^{25} +268^\circ$  (c, 1.3, chloroform). Calculated for  $C_{12}H_{12}O_7Br$ : C, 40.81%; H, 4.85%. Found: C, 40.98%; H, 4.95%) with 1,2,3,4-tetra-*O*-acetyl  $\beta$ -D-glucose, according to the procedure of Talley, Reynolds, and Evans (2).

(for example, No. 3, Table I). A sample of the disaccharide octaacetate<sup>f</sup> prepared by Talley, Reynolds, and Evans was deacetylated and oxidized as described previously (4)

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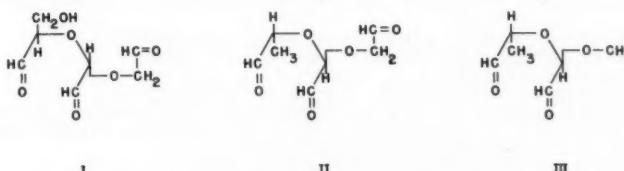
<sup>f</sup>Obtained through the kindness of Professor M. L. Wolfrom.

for isomaltose octaacetate. The rotatory power of the oxidation product (No. 2, Table I) showed that the disaccharide possesses the  $\alpha$ -D-linkage, rather than the  $\beta$ -D-linkage assigned (2).

A (1  $\rightarrow$  6)-mannobiose octaacetate (designated (1  $\rightarrow$  6)- $\beta$ -D-) was synthesized in the same manner by these earlier workers (2), and examination of this disaccharide\* (No. 4, Table I) showed that it too must be assigned the  $\alpha$ -D-linkage. This disaccharide has been obtained by acid reversion of D-mannose and partial hydrolysis of yeast mannan (5), its configuration having been confirmed earlier by the periodate oxidation method (4).

Two trisaccharides have been synthesized by Talley and Evans (6) through condensation of the  $\alpha$ -acetobromo derivative of their 6-O-D-mannopyranosyl-D-glucose with 1,2,3,4-tetra-O-acetyl-D-glucose or -D-mannose. These trimers may now be redesignated, therefore,  $O$ - $\alpha$ -D-mannopyranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranosyl-(1  $\rightarrow$  6)-D-glucose, and  $O$ - $\alpha$ -D-mannopyranosyl-(1  $\rightarrow$  6)- $\beta$ -D-glucopyranosyl-(1  $\rightarrow$  6)-D-mannose. The trisaccharides were thought (6) to be isomeric, or identical, with two oligosaccharides prepared (7) by acetolysis of the glucomannan from *Amorphophallus konjac*. Recently, however, it has been shown that the parent polysaccharide contains (1  $\rightarrow$  4)-, but not (1  $\rightarrow$  6)-, glycosidic linkages (8).

Reducing disaccharides which contain L-rhamnopyranose (6-deoxy-L-mannopyranose) as the non-reducing end unit have also been prepared by the Königs-Knorr reaction. Rutinose, the sugar moiety of the flavone glycoside, rutin, has been synthesized (9) from 2,3,4-tri-O-acetyl- $\alpha$ -L-rhamnopyranosyl bromide and 1,2,3,4-tetra-O-acetyl- $\beta$ -D-glucose in the presence of mercuric acetate (the Zempen modification (10)) and its linkage assigned a  $\beta$ -configuration. Similarly, the related disaccharide robinobiose, a component of the flavonoid robinin, has been synthesized and designated 6-O- $\beta$ -L-rhamnopyranosyl-D-galactose (11). On periodate oxidation these disaccharides theoretically should yield a trialdehyde (II,  $\alpha$ -L-anomer) which is closely related structurally to that (I) produced from (1  $\rightarrow$  6)-linked aldohexose disaccharides, or to the dialdehyde produced from the corresponding methyl L-rhamnopyranoside (III,  $\alpha$ -L-anomer). Examined by the oxidation procedure, rutinose† afforded a strongly levorotatory product (No. 5, Table I) which, by comparison with the products prepared from methyl 6-deoxy- $\alpha$ - and  $\beta$ -L-glycopyranosides (13) (Nos. 8 and 9, Table I), was to be expected for the  $\alpha$ -L-isomer. Confirmation of this possibility was provided by the fact that 6-O-(6-deoxy-



$\alpha$ -D-galactopyranosyl)-D-glucose (No. 6, Table I) on oxidation yielded a product having a specific rotation approximately equal and opposite to that produced from rutinose. In addition, the oxidation product derived from 6-O-(6-deoxy- $\beta$ -D-glycopyranosyl)-D-glucose (No. 7, Table I) possessed a negative specific rotation of much smaller magnitude than that shown by the  $\alpha$ -L- (or  $\alpha$ -D-) isomers, which parallels the properties of the corresponding methyl  $\beta$ -D- and  $\beta$ -L-glycosides (Nos. 9 and 10, Table I). These findings

\*Obtained through the kindness of Professor M. L. Wolfrom.

†Prepared by enzymic hydrolysis of rutin (12).

show, therefore, that rutinose is an  $\alpha$ -L- (rather than a  $\beta$ -L-) rhamnoside and, by analogy, that robinobiose most probably also is an  $\alpha$ -L-rhamnoside.\*

In most applications of the Königs-Knorr reaction it has been found that a Walden inversion accompanies replacement of the halide group, and the glycosidic linkage formed thus possesses a configuration opposite that of the parent glycosyl halide (16, 17, 18, 19, 20). Several reactions have been reported, however, in which the anomeric configuration of the product is the same as in the glycosyl halide used (for example, 21, 22, 23, 24, 25). Syntheses of the oligosaccharides considered above, using poly-O-acetyl- $\alpha$ -D-mannopyranosyl- or  $\alpha$ -L-rhamnopyranosyl-bromide, clearly represent yet other examples in which configuration is retained. The latter two glycosyl halides may also undergo replacement with inversion, nonetheless, since on methanolysis the respective  $\beta$ -glycosides (together with orthoesters) have been obtained (24, 26, 27). These conflicting results are related possibly to the fact that different reaction conditions have been used in preparing the two classes of compounds. For methyl glycoside formation, the methanol served also as the reaction medium (24, 26, 27), whereas a less polar solvent (benzene or chloroform) was used in synthesis of the disaccharides (2, 9, 11). Isbell and Frush have shown (24) that use of a diluent (for example, benzene or ether) alters the course of the methanolysis of tetra-O-acetyl- $\alpha$ -D-mannopyranosyl bromide, promoting synthesis of the  $\alpha$ -D-glycoside and a lower yield of the  $\beta$ -D-glycoside and orthoacetate. They suggested that the diluent interacts with an orthoester-type intermediate, formed with participation of the 2-O-acetyl group, permitting the reaction with methanol to proceed without a Walden inversion.† In the light of these observations, therefore, the formation of  $\alpha$ -D-mannosyl- and  $\alpha$ -L-rhamnosyl-disaccharides by the Königs-Knorr reaction is understandable.

The authors are grateful to Professor M. L. Wolfrom and Drs. G. L. Talbot and F. J. Simpson for the gift of samples, and to J. W. L. C. Christ and Sheila Lubin for technical assistance. Microanalyses were performed by M. Mazurek.

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\*The specific rotation of rutinose, when correlated with Hudson's observations on the configuration of disaccharides (14), suggests that the compound possesses the  $\alpha$ -L-linkage (15). Similarly, the specific rotations of the D-mannopyranosyl disaccharides considered above, are much more in accord with assignment of the  $\alpha$ -D-linkage, rather than the  $\beta$ -D-linkage, to these bioses.

†Alternatively, retention of configuration has been ascribed (20) to formation initially of a cyclic orthoester ion (17, 19) which undergoes further solvolysis, so that two successive Walden inversions occur. However, this mechanism does not account for the solvent effects noted above.

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**CATALYTIC ACTIVATION OF MOLECULAR HYDROGEN IN SOLUTION  
 BY CHLORORHODATE(III) COMPLEXES**

J. F. HARROD AND J. HALPERN

We have found that rhodium (III) chloride, in aqueous solutions containing hydrochloric acid, activates molecular hydrogen homogeneously. Its behavior is qualitatively very similar to that observed earlier (1) for palladium (II) chloride and the same procedure (i.e. determination of the rate of catalytic reduction of ferric chloride by measuring the volume of hydrogen taken up at constant pressure) was employed to study the kinetics. The results are summarized in Table I.

The kinetics of the catalyzed reduction of ferric chloride were found to be of the form

$$-d[H_2]/dt = k[H_2][\text{Rh(III)}].$$

Typical hydrogen uptake rate plots are shown in Fig. 1. Simultaneous spectrophotometric measurements confirmed that the hydrogen taken up is consumed in the reduction of

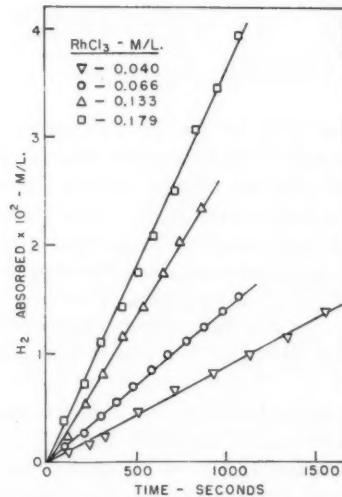


FIG. 1. Rhodium (III) chloride catalyzed reduction of ferric chloride at 80°, 450 mm Hg.

Fe(III) to Fe(II) and that the concentration of Rh(III) remains constant. The reaction under these conditions is clearly homogeneous (providing the HCl concentration exceeded 3 M, the reduction of Rh(III) to metallic Rh, a powerful heterogeneous catalyst, did not commence until the reduction of Fe(III) to Fe(II) was nearly complete), and since the concentrations of Rh(III) and of H<sub>2</sub> remain constant, the kinetics are of pseudo-zero order. Values of *k* are listed in Table I and are seen to be substantially independent of the concentrations of Fe(III), H<sub>2</sub>, and Rh(III). The slight dependence on the HCl concentration and the effects of added electrolytes follow much the same pattern as found for Pd(II) and are attributable to variations in the solubility of hydrogen (1). Measurements of *k* over the temperature range 61.5° to 85.0° (Table I) yielded a good Arrhenius plot fitted by,

$$k = 2.3 \times 10^{15} \exp[-25,200/RT] \text{ l. mole}^{-1} \text{ sec}^{-1}$$

corresponding to an entropy of activation of +9 e.u.

TABLE I  
Summary of kinetic data

Temp. (° C)	[RhCl <sub>6</sub> ] (m/l.)	[FeCl <sub>3</sub> ] (m/l.)	H <sub>2</sub> (mm)	[H <sub>2</sub> ] × 10 <sup>4</sup> (m/l.) <sup>a</sup>	Medium	Rate × 10 <sup>6</sup> (m l. <sup>-1</sup> sec <sup>-1</sup> )	<i>k</i> (l. m <sup>-1</sup> sec <sup>-1</sup> )
80.0	0.040	0.17	450	3.6	3 M HCl	9.0	0.63
80.0	0.066	0.17	450	3.6	3 M HCl	13.6	0.57
80.0	0.133	0.17	450	3.6	3 M HCl	27.0	0.56
80.0	0.133	0.085	450	3.6	3 M HCl	26.0	0.54
80.0	0.179	0.17	450	3.6	3 M HCl	36.0	0.56
80.0	0.067	0.17	192	1.5	3 M HCl	6.0	0.59
61.5	0.179	0.17	625	4.8	3 M HCl	7.0	0.081
68.4	0.133	0.085	570	4.4	3 M HCl	11.4	0.195
74.6	0.133	0.085	510	3.9	3 M HCl	19.0	0.36
85.0	0.067	0.085	380	3.1	3 M HCl	21.0	1.01
80.0	0.067	0.15	450	3.6	5 M HCl	12.8	0.53
80.0	0.067	0.17	450	3.6	3 M HCl; 2 M NaCl	5.4	0.22
80.0	0.067	0.17	450	3.6	3 M HCl; 2 M LiCl	9.0	0.37
80.0	0.067	0.085	450	3.6	3 M HCl; 2 M NaClO <sub>4</sub>	8.5	0.35
80.0	0.067	0.085	450	3.6	3 M HCl; 2 M HClO <sub>4</sub>	17.0	0.70

<sup>a</sup>Based on solubility of hydrogen in 3 M HCl estimated as described earlier (1).

The insensitiveness of the rate to the HCl concentration in the region where RhCl<sub>6</sub><sup>3-</sup> is the predominant species (2, 3) suggests that the major catalytic contribution is due to this species, although it is not possible to rule out some contributions also from lower chloro complexes (particularly RhCl<sub>6</sub>(H<sub>2</sub>O)<sup>2-</sup> which is probably present in appreciable concentrations). It seems likely that the mechanism is of the same type as proposed earlier (1, 4) for kinetically analogous reactions of hydrogen involving other metal ions and complexes (including PdCl<sub>4</sub><sup>2-</sup>) as catalysts. This involves heterolytic splitting of hydrogen by the catalyst in the rate-determining step with formation of a catalyst-hydride complex (in this case HRhCl<sub>6</sub><sup>3-</sup>) which is reoxidized in subsequent rapid reactions with the substrate.

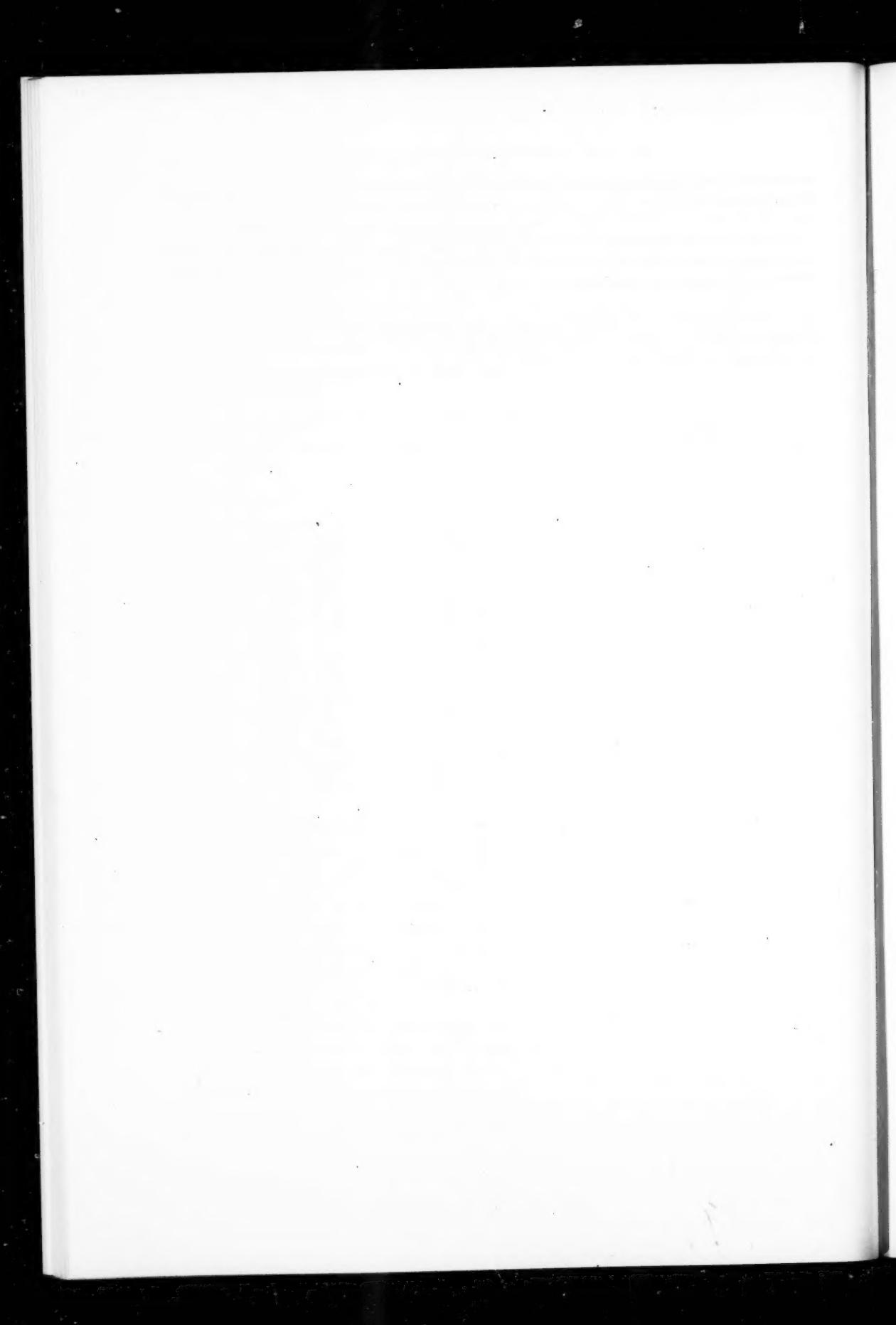
The abnormally high frequency factor of the present reaction is in contrast to the "normal" values ( $\sim 10^{11}$  l. mole<sup>-1</sup> sec<sup>-1</sup>) found for PdCl<sub>4</sub><sup>2-</sup> (1) and for most of the other catalytic species previously examined (5), and its significance is not clear. It may reflect the higher charge of the present catalytic species and imply some spreading out of the charge (resulting in a decrease in the electrostriction of the surrounding solvent) in the activated complex, such as would result from separation of one of the Cl<sup>-</sup> ligands. This

is consistent with earlier suggestions concerning the configuration of the activated complex in reactions of this type (4).

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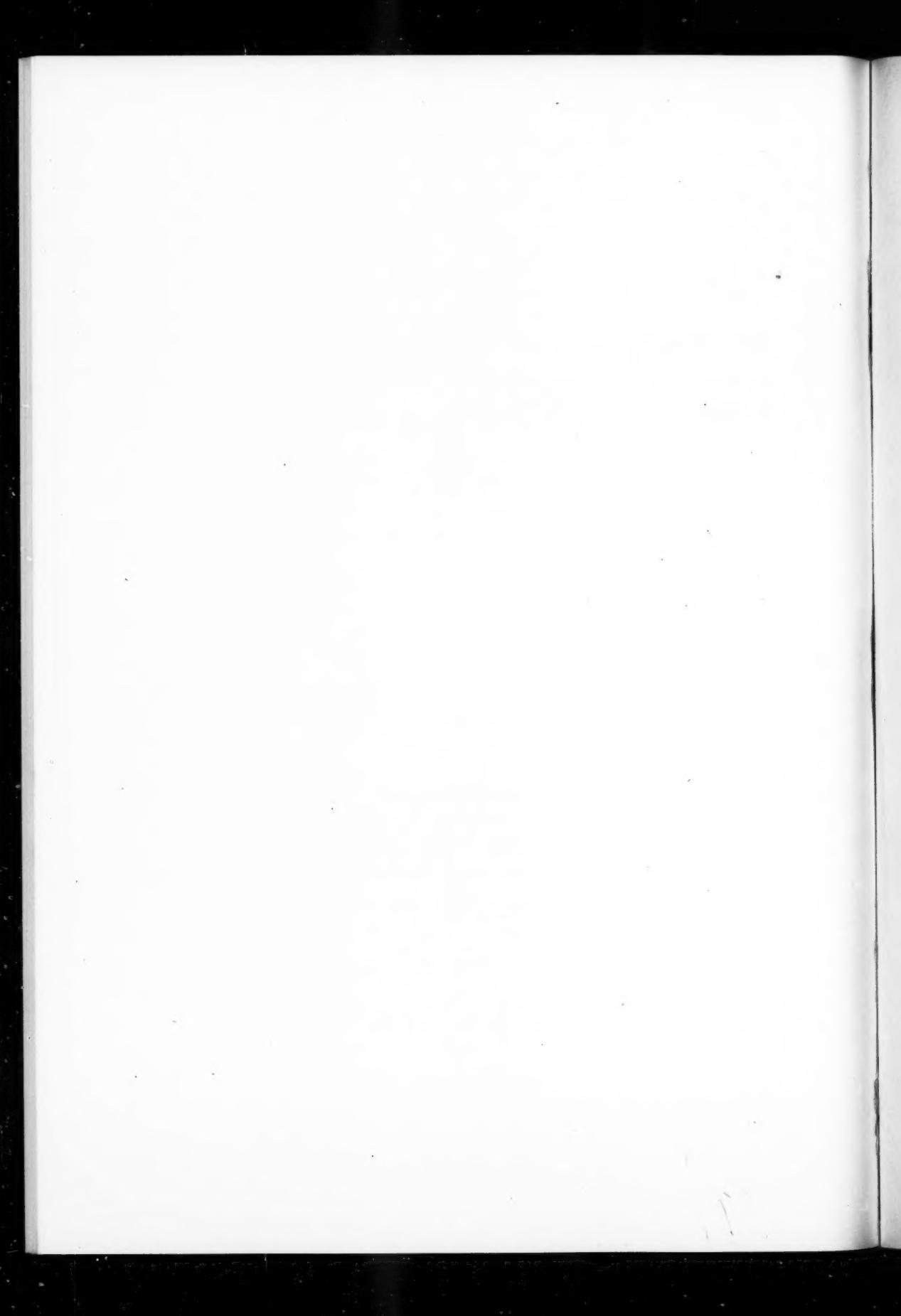
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